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**CALCULATIONS OF
QUANTITATIVE ANALYSIS**

BY CARL J. ENGELDER

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Fundamental principles of qualitative analysis; analysis of the cations; analysis of the anions; systematic analysis. Third Edition. Cloth; 6 by 9¼; 344 pages.

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CALCULATIONS OF QUANTITATIVE ANALYSIS

BY

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PREFACE

Theory and technique are the main objectives in a course of instruction in quantitative analysis. Technique is acquired more or less satisfactorily, with proper supervision, by practice in the laboratory, in working out the procedures and methods of analysis. Theory, the fundamental principles upon which the methods of analysis are based, in order to be applied, made usable and practicable, must be thoroughly understood, and this can be accomplished only through intensive study. In an exact science like analytical chemistry, the theoretical principles and concepts can be reduced to mathematical terms and hence the calculations involved in applying theory to practice constitute a very essential part of the study of quantitative analysis. Ample problem assignments must be made in a well-balanced course.

A logical, systematic sequence of problem assignments, in fifteen weekly sets, is presented in this book, to cover and supplement the usual more or less standard conventional semester's work in elementary quantitative analysis. Each problem set consists of twenty problems, a total of three hundred; discussion of theory, together with numerous illustrative examples, accompanies each problem set. The order of development is designed to keep abreast of the laboratory work.

Although many textbooks of quantitative analysis are supplied with problems, interspersed throughout the descriptive and experimental matter, the problems oftentimes depend upon and are made an integral part of the procedure of analysis there described. This book, "Calculations of Quantitative Analysis," aims to make stoichiometry a distinct yet correlated phase of the students' work, in which the calculations are applied from the theory to typical analysis. It is suggested that a weekly recitation period, preceded by assignments for home study, will best accomplish the purpose.

Odd-numbered problems, with answers, are intended for home assignments, by which the student can check the correctness of his method of solution of problems. Even-numbered problems, without answers, are suited for classroom work, quizzes or examinations. Answers to even-numbered problems are available in leaflet form, upon request, with proper authorization from publisher or author.

The book is divided into four parts. Part I covers introductory con-

siderations, arithmetical operations and reagents in general. Part II and Part III cover volumetric and gravimetric calculations respectively. If gravimetric technique is to be introduced in the laboratory before volumetric the problem sets of Part III will be found to be designed for this independent approach. The author followed the prevailing practice of introducing volumetric work before gravimetric. Part IV concludes with the applications that are made of analytical data, no matter whether the method of securing the data was volumetric or gravimetric.

The author has taken certain descriptive portions of the text from his "Calculations of Qualitative Analysis" and "Elementary Quantitative Analysis." The problems are new and original and have gradually accumulated by use in his classes over a period of years.

CARL J. ENGELDER

UNIVERSITY OF PITTSBURGH

March 1, 1939

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CALCULATIONS OF QUANTITATIVE ANALYSIS

PART I

INTRODUCTION

CHAPTER I

GENERAL CONSIDERATIONS

The purpose of quantitative analysis is to determine the amounts of the constituents present in a given sample of material. This object may be accomplished by either chemical or physical means, depending on the nature of the material and on the properties of the constituents to be determined. Generally the method of analysis is chemical, the determination being based on a suitable reaction which involves the constituent in question. The most important of the chemical methods of quantitative analysis are the gravimetric and the volumetric methods of determination. In the former, the constituent is isolated and weighed directly, usually in the form of a pure compound of known, definite composition. In the volumetric methods the constituent present is caused to react with an accurately measured volume of reagent the strength of which is definitely known.

Whatever the technique in carrying out a determination, the fundamental basis of the calculations of quantitative analysis rests firmly on the laws of chemical reactions. These are (1) the Law of Chemical Equilibrium and (2) the Law of Combining Weights. By suitable applications of the first-named law, the equilibrium relationships in a reacting system can be ascertained, the correct conditions for an accurate determination are established, and the extent or completeness of the reaction can be calculated. Applications and illustrations of equilibria will be referred to frequently in this book.

The Law of Combining Weights, together with the Law of Definite Proportions, is the most fundamental generalization in chemical science. The latter law states that in a chemical compound the constituents are always present in definite, constant proportions, whereas the Law of

Combining Weights states that in a chemical reaction, combination or reaction takes place by weights which are proportional to the atomic or molecular weights of the reacting constituents. Therefore, given the equation for a chemical reaction, we can calculate the weight of reagent required, as well as the weight of product formed in the reaction; or, conversely, if we measure the amount of reagent required or weigh the product resulting from the reaction we can, by direct proportion, calculate the amount of constituent present. A calculation based on such a direct proportionality between actual weights and atomic or molecular weights is known as a stoichiometric calculation. Such stoichiometric, or direct proportion, calculations are a necessary and important part of every quantitative determination; and, together with equilibrium calculations, they embrace practically all the calculations of this fundamental phase of chemistry.

The data, obtained in a quantitative analysis and used in the calculation of results, consist fundamentally of weights, and of measured volumes of solutions. The measurements are made by means of the analytical balance and the volumetric measuring apparatus, namely, flasks, pipettes and burettes. The operations or manipulations by which these necessary data are secured consist, therefore, of accurate weighing and careful measuring.

Since the object of a quantitative determination is to find the amount of pure constituent in a given sample, the calculation of the results, from the analytical data, resolves itself into finding in what ratio the pure constituent is present in the sample taken for analysis. Most commonly, the proportion by weight, rather than by volume, is desired. The relation is, then, numerically, a ratio of the weight of pure constituent to the weight of sample, i.e., $\frac{\text{Weight of pure constituent}}{\text{Weight of sample}}$.

If, for example, we find, by analysis, that a 0.2500-gram sample of a silver alloy contains 0.1250 gram of pure silver, then the ratio $\frac{0.1250}{0.2500}$, or 0.5000, gives the proportion of pure silver in the sample. It is to be strongly emphasized, at this point, that no matter by what chemical or physical method the determination is carried out, whether a gravimetric or a volumetric method of analysis is employed, the ultimate objective in any such analysis is to determine the weight of the pure constituent.

The final result is most frequently expressed in terms of percentage by weight, i.e., in parts per hundred parts of the sample. This leads to a simple, direct proportion, expressed thus:

$$\text{Weight of pure constituent: Weight of sample} = x : 100$$

in which x is the parts by weight of constituent in 100 parts of the sample. By cross-multiplication, the more usable expression is obtained:

$$\frac{\text{Weight of constituent}}{\text{Weight of sample}} \times 100 = \text{Percentage}$$

In the example cited, the percentage of silver in the alloy is calculated thus:

$$\frac{0.1250}{0.2500} \times 100 = 50.00 \text{ per cent}$$

Instead of reporting the final result in terms of percentage, it might be reported in parts per thousand, per ten thousand or even, as in the case of the determination of traces, in parts per million. In fact, in the special field of precious-metal analysis, silver would be reported, not as percentage, but rather in parts per thousand. For this the term "fineness" is used; the alloy under consideration would be spoken of as being 500.0 fine, or as having a "fineness" of 500.0.

ERRORS, PRECISION AND ACCURACY

How accurate are the results of a quantitative analysis? How precise are the data obtained in the measurements? What are the sources of error and how can they be evaluated and minimized? These are questions constantly asked by the alert, thoughtful worker.

Errors arise from various sources, such as weighings and burette readings, inaccurately calibrated weights and volumetric apparatus, sheer carelessness in technique, inherent errors of the method itself, and personal errors due to the individual's observations. The magnitude of these errors can best be appreciated by considering the precision of the measurements.

Precision. By precision is understood the agreement among themselves of a series of measurements, calculations or results. In quantitative analysis the precision of a series of values is usually obtained from the average or mean deviation. To do this, the set of values is averaged and, from this average, the deviation of each individual value is obtained. These deviations from the average are then averaged, by which the average deviation from the average of the values is obtained. The result is expressed as a ratio, either in parts per hundred as percentage or else in parts per thousand. An illustration will make this clear.

Example 1. Calculate the precision, in percentage and in parts per thousand, of the following series of burette readings: (a) 30.25 cc.; (b) 30.20 cc.; (c) 30.15 cc.; (d) 30.23 cc. The average of the burette

readings is the sum divided by the number of readings, namely, $120.83 \div 4$, or 30.21 cc. Taking the difference between this average and each reading gives the deviations (a) 0.04 cc., (b) 0.01 cc., (c) 0.06 cc., (d) 0.02 cc. and an average deviation of 0.032 cc. Then

$$\frac{0.032}{30.21} \times 100 = 0.105 \text{ part per hundred (per cent)}$$

and

$$\frac{0.032}{30.21} \times 1000 = 1.05 \text{ parts per thousand}$$

The average precision is therefore approximately 0.1 of 1 per cent, or 1 part per thousand.

In the above example, all four observations have been retained and used in the computation. The individual precision of each might be calculated similarly. But suppose there had been a fifth reading, deviating considerably from the other four. The important question to decide in any series of values is what values to reject and not to include in the calculation. This matter is usually governed by the known precision of the measurement.

Accuracy. By accuracy is meant the agreement of a single result or the average of two or more results with the known correct result. The error in a result is the difference between the observed or calculated value or values and the true value. Thus, suppose the known percentage of constituent in a certain sample is 25.00 per cent and a student reports the values 24.90 per cent and 24.95 per cent, respectively. The reported results differ from the true value by 0.10 and 0.05 per cent. The errors made, expressed as percentage error, are therefore

$$\frac{0.10}{25.00} \times 100 = 0.4 \text{ per cent}$$

and

$$\frac{0.05}{25.00} \times 100 = 0.2 \text{ per cent}$$

Expressed as error in parts per thousand the errors are

$$\frac{0.10}{25.00} \times 1000 = 4 \text{ parts per thousand}$$

and

$$\frac{0.05}{25.00} \times 1000 = 2 \text{ parts per thousand, respectively}$$

Suppose four different silver-alloy samples are given to four students for analysis, and they report, as averages of their individual results, 24.95, 49.95, 74.95 and 99.95 per cent, respectively, the true content being 25.00, 50.00, 75.00 and 100.00 per cent. The absolute error made by each student is the same, namely 0.05. But the percentage errors are 0.2, 0.1, 0.05 and 0.025 respectively.

Significant Figures. Significant figures are the digits which when placed in order give the value to a number. Thus in the quantity represented by the number 635, the digits 6, 3 and 5 are significant figures. Zeros are used in some cases to locate the decimal point, in other cases they may be significant figures. In the number 30.25 the zero is a significant figure; in 0.015 the zeros are not significant but show the order of magnitude represented by the other digits. Zeros following other digits may or may not be significant.

The ordinary analytical balance weighs to one-tenth of a milligram, that is, to the fourth decimal place; hence only four digits to the right of the decimal point, in the weight of an object, are significant. A burette can be estimated to one one-hundredth of a cubic centimeter; hence two digits to the right of the decimal point are significant.

Computation Rules. In any calculation, in order that the result may express the degree of precision, the correct number of significant figures should be retained, and all others discarded. In general, only as many significant figures should be retained in a number as will give one uncertain figure. In rejecting uncertain figures the last figure retained should be increased by 1 if the discarded figure is 5 or more. Thus, if in the number 4.527 the last figure is uncertain the value 4.53 is to be recorded.

Addition and Subtraction. In adding or subtracting numbers, the rule is to retain in each number only such significant figures as correspond to the last digit in the number having the least number of significant figures to the right of the decimal point. An example will illustrate this rule.

Example 2. It is desired to find the sum of the weights of three objects. Suppose that three objects are carefully weighed on an analytical balance to the fourth decimal place, that is, to tenths of a milligram, the weights being 17.9000 grams, 4.5300 grams and 0.0560 gram, respectively. In this case, the zeros in the first and second numbers and the zero following the 6 in the third number are all significant and are therefore retained, the desired sum being, as tabulated in case I, below, 22.4860 grams.

Suppose, however, on the other hand, that the first object is roughly weighed to the nearest tenth of a gram, 17.9 grams being recorded, that

the second object is weighed to the nearest hundredth of a gram, 4.53 grams and the weight of the third object being recorded as 0.056 gram. Since the number 17.9 contains but one significant figure to the right of the decimal point, the other fractional parts of a gram not being determined, this number controls the discarding of significant figures from the other two quantities. The numbers to be added are therefore 17.9, 4.5 and 0.1 gram (the number 0.056 being modified in accordance with the rule that, if the figure to be discarded is 5 or more, the preceding figure is increased by 1).

Comparison of these two cases is shown in the following tabulation.

Case I	Case II
17.9000	17.9 retained as 17.9
4.5300	4.53 changed to 4.5
0.0560	0.056 changed to 0.1
<hr/> 22.4860 grams	<hr/> 22.5 grams

Multiplication and Division. In multiplying and dividing, the precision of the result cannot be greater than the precision of the quantity containing the least number of significant figures. Therefore, as many significant figures should be retained as are contained in the quantity of the least accuracy, the quantity with the least number of significant figures. In a series of multiplications or divisions superfluous figures should be discarded at each operation and not carried throughout several such steps. The final result will then appear with the correct number of significant figures.

EXPONENTS

~~The labor of counting figures to the left or right of the decimal point can be eliminated by the use of exponents.~~ In addition to economy of space, a glance at the exponent gives an immediate insight into the magnitude of the number. In data concerning solubility, equilibrium constants and in general in many of the data of the exact sciences, even though the magnitudes may be extremely large or small, the values are seldom obtained with a precision extending to even the fourth significant figure.

The magnitude of a quantity is expressed in the exponential form by writing the digits as coefficients multiplied by 10 raised to the proper power. Thus, the number 1000, which is the product of $10 \times 10 \times 10$, or ten cubed, is written exponentially 1×10^3 . The number 0.001, the product of $0.1 \times 0.1 \times 0.1$, is written 1×10^{-3} . The number 7000 becomes 7×10^3 , and 0.007 becomes 7×10^{-3} . The simple rules

for exponents and coefficients in converting ordinary numbers into the exponential form are these:

1. For numbers greater than unity, the exponent acquires the same value as the number of zeros in the ordinary number. In the example given, three zeros are found; therefore the exponent is 3.

2. For numbers less than unity, i.e., for decimal fractions, the exponent, with a negative sign, is one more than the number of zeros which follows the decimal point. In converting the number 0.007, the exponent is -3 .

3. According to the convention adopted in this book, the coefficients are treated in the following manner. When more than one significant figure is given, followed or preceded by zeros, the first significant figure is placed before the decimal point, the other significant figures following the decimal point. In view of this convention in the location of the decimal point, the value of the exponent must be adjusted. For example, the number, 504000, when expressed according to rule (1), is 504×10^3 , but according to the convention of placing one significant figure to the left of the decimal point, the quantity is written 5.04×10^5 . Likewise, the number 0.000504 becomes 5.04×10^{-4} .

By using the exponential form of expression, the arithmetical operations of multiplication, division, etc., are greatly simplified.

Multiplication by Use of Exponents. To multiply two or more quantities, the numbers are first expressed exponentially. The coefficients are then treated in the ordinary way and the exponents are added algebraically.

Example 3. Multiply 45,000 by 0.051.

Since 45,000 becomes 4.5×10^4 and 0.051 becomes 5.1×10^{-2} we have by multiplying the coefficients and adding the exponents

$$\begin{aligned} 45,000 \times 0.051 &= (4.5 \times 5.1) \times 10^{4-2} \\ &= 22.95 \times 10^2 \\ &= 2.295 \times 10^3 \\ &= 2.3 \times 10^3 \\ &= 2300 \end{aligned}$$

Division by Use of Exponents. When dividing two quantities after expressing them in the exponential form, the coefficients are divided in the ordinary manner, and the exponents are subtracted algebraically.

Example 4. Divide 3730 by 15.21.

$$\begin{aligned}\frac{3730}{15.21} &= \frac{3.730 \times 10^3}{1.521 \times 10^1} \\ &= 2.452 \times 10^2 \\ &= 245.2\end{aligned}$$

When raising numbers to any required power, the exponents are doubled for squaring, trebled for cubing, etc., the coefficients being squared, cubed, etc., in the ordinary way.

Example 5. Square the number 6.0×10^3 .

$$\begin{aligned}(6.0 \times 10^3)^2 &= (6 \times 10^3) \times (6 \times 10^3) \\ &= 36 \times 10^{3 \times 2} \\ &= 36 \times 10^6 \\ &= 3.6 \times 10^7\end{aligned}$$

When extracting the square root, divide the exponent by 2, and when extracting the cube root, divide the exponent by 3, treating the coefficients in the usual manner. If the exponent is an odd number, increase it by 1 and compensate for this in the coefficient.

Example 6. Extract the square root of 1.6×10^{-5} . Changing this to an exponential value with an even exponent

$$\begin{aligned}\sqrt{1.6 \times 10^{-5}} &= \sqrt{16 \times 10^{-6}} \\ &= 4 \times 10^{-3}\end{aligned}$$

The extraction of roots becomes a comparatively simple matter when logarithms are used, as explained on page 10.

LOGARITHMS

The solving of problems and of the results of determinations from analytical data is greatly facilitated by the use of logarithms, and it is strongly advised that students employ this method. To those not familiar with logarithms, it may be said that many hours of tedious long-hand computation may be saved by acquiring a working knowledge of this very helpful mathematical device.

A logarithm is an exponent which must be applied to a number, known as the base, in order to produce any given number. In the common or Briggsian system of logarithms, the base is 10. Thus in the equation

$$10^{2.0000} = 100$$

the exponent 2.0000 is the logarithm of 100, when the base is 10. The above equation, in terms of logarithms, can then be written:

$$\log_{10} 100 = 2.0000$$

which states that the logarithm of 100 to the base 10 is 2.0000. The relation of exponential to logarithmic forms for simple, whole numbers as exponents is shown in Table I.

TABLE I

Number	Exponential Form	Logarithm
1,000,000	10^6	6
1,000	10^3	3
100	10^2	2
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.01	10^{-2}	-2
0.001	10^{-3}	-3
0.000001	10^{-6}	-6

Note that the logarithm of 10 is 1, that of 1 is 0 and that for negative exponents there result corresponding negative logarithms.

A logarithm is made up of two parts: the mantissa, placed to the right of the decimal point, and found in logarithmic tables; and the characteristic, which is placed to the left of the decimal point. The mantissa gives the antilogarithm or the number of which it is the logarithm; the characteristic locates the decimal point in the antilogarithm. Thus the logarithm of 217 is 2.3365, where 2 is the characteristic and 0.3365 is the mantissa. In four-place tables of logarithms, the mantissa is given to four significant places. The following rules apply in determining the characteristic:

1. If there are n digits before the decimal point, the characteristic is represented by a number equal to $n - 1$. Thus the number 217 has $3 - 1$, or 2, as the characteristic of its logarithm.

2. If there are no digits before the decimal point and no zeros before the significant figures after the decimal point, the characteristic is $\bar{1}$, or $9 - 10$. If there are no digits before the decimal point, and n zeros before the first significant figure after the decimal point, the characteristic is $\bar{1} + (-n)$ or $(9 - n) - 10$. It is to be noted that the char-

acteristic only is affected by the negative sign, the mantissa retaining a positive value.

The following examples will illustrate the use of the logarithm tables in finding logarithms.

Example 7. Find the logarithm of 5326.

The characteristic is 3 since there are 4 digits before the decimal place. In the table of logarithms in the Appendix locate 53 in the "natural-numbers" column, and move horizontally to the right until, under the "2" column, the figures 7259 are found. This is the mantissa of 5320. Moving further to the right along the same line the figure 5 is found under column 6 of "Proportional Parts." This figure, 0005, shows how much greater the logarithm of 5326 is than that of 5320. The logarithm of 5326 is therefore $3.7259 + 0.0005$, or 3.7264.

Example 8. Find the logarithm of 0.0002457.

The characteristic is $\bar{4}$ or $6 - 10$. The mantissa is found by locating 24 in the "natural numbers" column and moving horizontally to the "5" column. To the figures there found, 3892, must be added the proportional part under "7," giving 3904 as the value for the mantissa. The logarithm is therefore $\bar{4}.3904$, or $6.3904 - 10$.

Use of Logarithms in Mathematical Operations. The operations of multiplication and division, and their extensions to raising numbers to any desired power, or, conversely, in extracting roots, are most readily accomplished by the use of logarithms. For multiplication and division the process consists in converting the given numbers to their logarithms, then performing the indicated addition or subtraction, and finally converting the sum or difference of the logarithms to ordinary numbers. Finding the number corresponding to a logarithm is obviously the reverse of the process of finding a logarithm. This involves the use of a table of antilogarithms and is illustrated in the following example.

Example 9. Find the antilogarithm of 2.1768.

Using the table of antilogarithms in the Appendix, locate the number 17 in the "logarithms" column. Move horizontally to the "6" column, where 1500 is found. Move further to the right until, under "Proportional Parts," column "8" is reached. The figure 3 found there is added to 1500, giving 1503. The characteristic 2 means that there are three digits to the left of the decimal point. The required number is therefore 150.3.

Extraction of Square and Cube Roots. The simplest manner of extracting square and cube roots is by the use of logarithms. Since logarithms are exponents, the rules given in the section on exponents will govern the method used. This is illustrated by the following examples.

Example 10. Find the square root of 504.7.

The logarithm of 504.7 is 2.7030. Dividing this latter quantity by 2 gives 1.3515, the logarithm of the square root. The desired number is, therefore, 22.5.

Example 11. Find the cube root of 0.0356.

The logarithm of 0.0356 is $\bar{2}.5514$, or $8.5514 - 10$. It is desirable on division to obtain a quotient which will retain the quantity -10 . Hence, the logarithm is adjusted to $28.5514 - 30$. Division by 3 gives the value $9.5171 - 10$. The antilogarithm, the cube root of 0.0356, is 0.329.

Interconversion of Exponential Numbers. It is sometimes desired to express quantities in the exponential form so that the coefficient shall be 1. This transformation necessitates the use of logarithms. Calculations of this kind are illustrated in the following examples.

Example 12. Express the quantity 6.2×10^4 in the pure exponential form.

In order to transfer the coefficient, 6.2, to the exponent, the logarithm of 6.2 is added to the logarithm of 10^4 .

$$\begin{aligned}\log (6.2 \times 10^4) &= \log 6.2 + \log 10^4 \\ &= 0.7924 + 4 \\ &= 4.7924 \\ &= 4.8\end{aligned}$$

From the fact that logarithms are exponents it is obvious that

$$6.2 \times 10^4 = 1 \times 10^{4.8}$$

Example 13. Convert 7.2×10^{-5} to the pure exponential form.

$$\begin{aligned}\log (7.2 \times 10^{-5}) &= \log 7.2 + \log 10^{-5} \\ &= 0.8573 + (-5) \\ &= -4.1\end{aligned}$$

Therefore

$$7.2 \times 10^{-5} = 1 \times 10^{-4.1}$$

The reverse process affords no difficulties when positive exponents are involved, but the operation is somewhat more complicated with negative exponents. Suitable examples of both types follow.

Example 14. Express $1 \times 10^{6.45}$ as a mixed number.

In the quantity $1 \times 10^{6.45}$ the exponent 6.45 is a logarithm with a characteristic of 6 and a mantissa of 0.45. In order to retain in the

exponent the whole number, 6, it is necessary to find the antilogarithm of 0.45 and use it as the coefficient.

From the antilogarithm tables, the antilogarithm of 0.45 is 2.8.

Therefore,

$$\begin{aligned} 1 \times 10^{6.45} &= 1 \times 10^{0.45} \times 1 \times 10^6 \\ &= 2.8 \times 10^6 \end{aligned}$$

Example 15. Convert $1 \times 10^{-7.63}$ into a mixed number.

In the discussion of the nature of logarithms it was stated that the mantissa must have a positive value. In the exponent or logarithm -7.63 , the mantissa as well as the characteristic is negative, and in order to convert the value -0.63 into a positive mantissa, 0.63 is subtracted from 1.00 giving as a positive mantissa 0.37 and -8 as the new characteristic, or

$$1 \times 10^{-7.63} = 1 \times 10^{-8} \times 10^{0.37}$$

From the antilogarithm table it follows that

$$10^{0.37} = 2.3$$

The converted quantity can now be expressed as a mixed number, with a positive coefficient and an exponent consisting of a negative whole number.

Therefore

$$1 \times 10^{-7.63} = 2.3 \times 10^{-8}$$

The calculation of pH values, discussed in Chapter V, involves the finding of the logarithm of reciprocals. Here, the expression of quantities in the pure exponential form is often highly desirable. The following examples illustrate the method of procedure.

Example 16. Calculate the value of $\log \frac{1}{1 \times 10^{-6}}$.

$$\begin{aligned} \log \frac{1}{1 \times 10^{-6}} &= \log 1 - \log 10^{-6} \\ &= 0 - (-6) \\ &= 6 \end{aligned}$$

PROBLEM SET 1

PRECISION, ACCURACY, ERRORS, MATHEMATICAL COMPUTATIONS

1. Using the ordinary analytical balance, three students weighed the same object and reported the weight as 6.123 grams, 6.1230 grams and 6.12300 grams, respectively. Which value is correctly reported? *Ans.* 6.1230.

2. Volumes of solutions were reported having been measured as follows: (a) 16.2 cc. from a 100-cc. measuring cylinder; (b) 10 cc. from a 10-cc. transfer pipette; (c) 32 cc. from a 50-cc. burette. How should each have been reported?

3. If (a) in measuring 10.00 cc., an error of 0.10 cc. is made, what is the percentage error in the measurement? If (b) the same error is made in measuring 25.00 cc.? If (c) in measuring 50.00 cc.?

Ans. (a) 1.00 per cent.

(b) 0.40 per cent.

(c) 0.20 per cent.

4. What weight of constituent should be found in a series of analyses in which the weight of sample is 0.5000 gram and the percentage of constituent present is: 1, 10, 30, 80 and 98 per cent respectively?

5. Suppose that in a gravimetric determination, run in triplicate, the weights of the precipitates are respectively 0.8112, 0.8106 and 0.8100 gram. If in each the weight of precipitate is multiplied by the factor 0.4116 and divided by the weight of sample, 0.5000 gram, what is the percentage of constituent in the sample, and what is the precision in parts per thousand? Should any of the results be rejected if the precision of the method is 3 parts per thousand?

Ans. (a) 66.77; 66.73; 66.68 per cent.

(b) Deviation of 0.6; 0; 0.7 part per thousand.

(c) No.

6. The result of an analysis run in triplicate gave 70.12, 70.65, and 70.24 per cent of constituent in the sample. (a) If the precision of this particular determination is 0.2 of 1 per cent, what value, if any, should be rejected? (b) Calculate the deviation of each result from the mean. (c) If the correct result is 70.30 per cent, what is the percentage error made in each run?

7. In a certain analysis a chemist took too small a weight of sample so that the result corresponded to only 0.0050 gram of constituent. (a) If an error of 0.1 milligram was introduced in the analysis, how large a percentage error has been made? (b) If on the other hand with a much greater weight of sample the result corresponded to 0.5000 gram of constituent and the same error of 0.1 milligram was introduced, what was the percentage error in this case?

Ans. (a) 2.0 per cent; (b) 0.02 per cent.

8. The analysis of a certain material gave 30.12 per cent and 29.97 per cent. (a) What is the precision of the analysis expressed in parts per thousand? (b) If the true value is 30.00 per cent, what is the percentage error of each determination?

9. If, in a certain titration procedure requiring 35.00 cc. of titrating solution, each cubic centimeter of which is equivalent to 0.005394 gram of silver, the end point is overstepped by two drops (0.1 cc.), what is the error in terms of grams of silver? What is the error, if, in a similar titration, the titrating solution has a silver value of 0.05394 gram per cubic centimeter?

Ans. 0.54 milligram; 5.4 milligrams.

10. Suppose that in a quantitative determination it is desirable that the weight of constituent determined should not be less than 1 centigram (0.0100 gram). What weight of sample should be taken, if the constituent is known to be present in the sample in the approximate percentages: 1; 10; 25; 50; 75; 95?

11. Duplicate results, obtained in determining a certain constituent, gave 0.2167 gram and 0.2160 gram of the constituent in 0.2552 gram of the sample. Calculate (a) the percentage of the constituent in the sample; (b) the deviation from each other, in percentage, of the two results; (c) the deviation from each other of the percentage, expressed in parts per thousand.

Ans. (a) 84.91 and 84.64 per cent.

(b) 0.27 per cent; (c) 3.2 parts per 1000.

12. Successive weighings of an ignited precipitate gave the following values: 0.3657, 0.3654, 0.3653 gram. What is the deviation from the mean (a) in milligrams; (b) in parts per thousand?

13. If 0.7658 represents the weight in grams of ignited precipitate obtained in a gravimetric determination, 0.4116 a factor, by which this weight is multiplied in order to give the weight of constituent, and the weight of sample used is 0.4789 gram, how would you represent the percentage of constituent, with respect to the number of significant figures retained?

Ans. 65.82 per cent.

14. Rewrite each factor in the following indicated equation in the exponential form and solve for x .

$$\frac{0.00131 \times 0.00131}{0.0986} = x$$

15. Solve for x in the following equations:

$$(a) \frac{1.2 \times 10^{-14}}{2.3 \times 10^{-11}} = x. \quad \text{Ans. (a) } 5.2 \times 10^{-4}.$$

$$(b) \frac{1.2 \times 10^{-14}}{5.0 \times 10^{-6}} = x. \quad (b) 2.4 \times 10^{-9}.$$

$$(c) \sqrt{1.2 \times 10^{-14}} = x. \quad (c) 1.1 \times 10^{-7}.$$

16. Solve for x in the following equations:

$$(a) x \times 3.5 \times 10^{-11} = 1 \times 10^{-13.92}$$

$$(b) x \times 1 \times 10^{-6.96} = 1 \times 10^{-13.92}$$

$$(c) x \times 8.1 \times 10^{-4.72} = 1 \times 10^{-13.92}$$

17. Quantities typical of the data of quantitative analysis are given below, properly arranged. Perform the indicated operations, using logarithms:

$$(a) \frac{0.7658 \times 0.4116}{0.4789} \times 100 = x. \quad \text{Ans. (a) } 65.83.$$

$$(b) \frac{0.2548 \times \frac{107.88}{169.89}}{30.00} = x. \quad (b) 0.005394.$$

$$(c) \frac{0.1620}{30.00 \times 0.05300} = x. \quad (c) 0.1019.$$

18. Convert the following quantities into pure exponents:

$$(a) 1.2 \times 10^{-14}.$$

$$(b) 3.8 \times 10^{-4}.$$

$$(c) 1.8 \times 10^{-5}.$$

19. Calculate the value of:

$$(a) \log \frac{1}{6.2 \times 10^{-4}}$$

Ans. (a) 3.2.

$$(b) \log \frac{1}{7.63 \times 10^{-8}}$$

(b) 7.12.

$$(c) \log \frac{1}{1 \times 10^{-6.96}}$$

(c) 6.96.

20. With logarithm tables, a slide rule (if you are familiar with its use) and watch at hand, time yourself for the following indicated operations using (a) long-hand computation, (b) log tables, (c) slide rule.

$$\frac{35.65 \times 0.1086 \times 0.03546}{0.5000} \times 100 = ?$$

With regard to the retention of the correct number of significant figures in the final result, how do the three results agree? Should slide-rule computations be employed in computing the results of a quantitative analysis?

CHAPTER II

THE REAGENTS OF QUANTITATIVE ANALYSIS

Inasmuch as chemical methods of quantitative analysis are based on reactions which are brought about, in general, by adding reagents to the material undergoing analysis, the selection, preparation and use of the proper reagents deserve our first attention. In fact, from this point of view the whole subject of quantitative analysis may seem to consist of the correct use of reagents. Every analytical chemical laboratory must be adequately supplied with a wide variety of reagents and it is the business of the analytical chemist to prepare them properly and to use them correctly. In an institutional laboratory some of these reagents are prepared in advance and supplied to the laboratory as shelf reagents whereas others must be prepared individually by each student.

The reagents consist of solids, gases and liquids, and have a variety of uses. Among the solids may be mentioned such substances as Na_2CO_3 , Na_2O_2 and KHSO_4 , used as fusion agents for rendering soluble the more refractory samples, and metals such as zinc and cadmium used as reducing agents. As examples of gases may be cited H_2S for the precipitation of sulfides, and carbon dioxide and nitrogen for maintaining inert atmospheres. The liquid reagents may be either pure liquids, namely, organic solvents and extractants such as ether, alcohol, acetone, etc., or else aqueous solutions prepared, in turn, by dissolving gases, liquids or solids in water or by diluting the more concentrated solutions. It should be pointed out that with regard to aqueous solutions, their strength is for the most part only approximately known, whereas, for the solutions used for titration in the volumetric methods of analysis, the strength must be accurately determined by a special process known as standardization; only after the strength is accurately known, are such solutions referred to as "standard" solutions.

The uses to which these reagents are put, based on the kind of reactions involved, may be briefly summarized as follows:

1. For dissolving samples, residues and precipitates.
2. For acidifying, neutralizing or rendering a solution basic.
3. For precipitating.
4. For oxidizing or reducing.

METHODS OF DESIGNATING THE STRENGTH OF SOLUTIONS

In the preparation of solutions of the many reagents employed, the experimenter must decide upon a suitable strength so that the proper amount of solute may be taken for the preparation of the desired quantity of reagent and upon a system of expressing the strength of the reagent. There are a number of methods in common use for expressing the strength of solutions and it is important to understand these designations. They are:

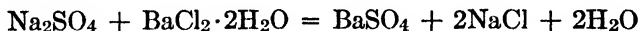
1. Solutions of empirical strength.
2. Volume-ratio designation.
3. Percentage by weight of solute.
4. Specific gravity or density.
5. Molar and molal solutions.
6. Normal solutions.
7. Titre designation.

These solutions will now be more fully described in connection with typical illustrative calculations involved either in their preparation or in their use.

1. Empirical Solutions. A number of reagent solutions are made of a strength best suited, by experience, for a particular purpose. The strength is frequently indicated in grams of solute per liter of solution. For example, a solution made by dissolving 20 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water and diluting to a liter is found well suited for the precipitation of BaSO_4 .

Example 1. How many cubic centimeters of a reagent containing 20 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter are required to react with 0.2467 gram of pure Na_2SO_4 ?

The reaction is:



By direct proportion, the ratio by weight is

$$\underset{(244.31)}{\text{BaCl}_2 \cdot 2\text{H}_2\text{O}} : \underset{(142.05)}{\text{Na}_2\text{SO}_4} = x : 0.2467$$

in which x is the total weight of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ required by 0.2467 gram of Na_2SO_4 . Solving this equation we find x to be 0.4240 gram. Since in 1000 cc. there are 20 grams of reactant, each cubic centimeter will contain 0.02000 gram and, since 0.4240 gram is required, the volume needed will be $0.4240 \div 0.02000$, or 21.2 cc.

2. Designation by Means of the Volume-Ratio. Occasionally one encounters, in following a procedure of analysis, instructions like "acidify with a 1 : 2 hydrochloric acid solution" or "neutralize with 1 : 9 ammonium hydroxide." A 1 : 2 HCl solution means a reagent made by diluting one volume of "concentrated" hydrochloric acid with two volumes of water. Such reagents are used for only the roughest work. The strength is not known accurately and the use of this designation is to be discouraged as unscientific.

3. Percentage by Weight Solutions. Under this designation, two types of reagents are referred to, namely (a) those made by dissolving a specified weight of solid solute and (b) the common neutralizing agents, namely ammonium hydroxide and hydrochloric, nitric and sulfuric acid. With respect to the first type, when referring to, let us say, "a 10 per cent solution of NaCl," the meaning is somewhat ambiguous, because such a solution might be made in any one of the following ways, namely, by dissolving:

1. 10 grams of NaCl and diluting to make 100 cc. of solution.
2. 10 grams of NaCl in 100 cc. of water.
3. 10 grams of NaCl in 100 grams of water.
4. 10 grams of NaCl in 90 grams of water so that the total weight of the solution is 100 grams.

Obviously only the last method will give a true 10 per cent solution by weight, though it is simpler and quicker to prepare the solution by the first or second method. The exact, scientific designation applies to the last type. Note that in preparing such a 10 per cent solution by dissolving 10 grams of NaCl in 90 grams of water, the total volume is not 100 cc.; nor is it 90 cc. The volume is dependent upon the expansion or, in special cases, the contraction of the liquid when a solute is added, and, of course, upon the temperature.

In designating the strength of the four common reagents mentioned under the second type, the percentage by weight of the pure (gaseous) solute may be employed, though usually the specific gravity of the solution is used instead. Nevertheless the percentage by weight is involved in the computations since these reagents are prepared by diluting the more concentrated ones. This type of reagent is discussed under the next heading.

4. Designation of Strength by Means of Specific Gravity. Reference to the density tables for HCl, HNO₃, H₂SO₄ and ammonia solutions, to be found in the Appendix, will show the variation of the specific gravity with the percentage by weight of the solute. It will be noted that, in the case of HCl the solute, hydrogen chloride, will dissolve in water,

at 15° C., until the resulting solution attains a specific gravity of 1.200 and contains 39.11 per cent by weight of pure HCl. Ordinary "concentrated" hydrochloric-acid solution will be considered in this book to have a specific gravity of 1.19 and to contain 37.23 per cent of HCl by weight.

In the cases of HNO_3 and H_2SO_4 , the solutions are formed by the oxides reacting with water, so that a 100 per cent solution is possible, corresponding to specific gravities of approximately 1.520 and 1.8385, respectively. These solutions, moreover, are capable of dissolving additional amounts of the oxides forming thereby fuming nitric and fuming sulfuric acids. The so-called concentrated nitric acid usually dispensed in the laboratory contains approximately 70 per cent of HNO_3 and its specific gravity, for the purposes of calculation, may be taken as 1.420. The laboratory concentrated H_2SO_4 is usually of 1.840 specific gravity corresponding to 95.60 per cent of H_2SO_4 .

With "aqua ammonia" solutions, produced by the reaction of NH_3 with the solvent, water, to form NH_4OH , the percentage of solute is given in the density table in terms of NH_3 rather than NH_4OH . "Concentrated" ammonium hydroxide, as sold by the manufacturer, has a specific gravity of about 0.900, containing the equivalent of 28.33 per cent of NH_3 .

Dilution Calculations. In order to show how the percentage by weight of the solute and the specific gravity of the solution enter into the calculations involved in the preparation and use of these neutralizing reagents, the following illustrative problems are presented.

Example 2. Suppose a laboratory procedure calls for the use of a hydrochloric-acid solution of specific gravity of 1.10. How much water should be added to 50 cc. of the "concentrated" reagent (specific gravity 1.19, containing 37.23 per cent by weight of HCl) in order to prepare a dilute solution of the required strength?

The problem resolves itself, algebraically, into finding the relationship between the specific gravities and percentages by weight so that the weight and hence the volume of water required for dilution can be calculated. Upon dilution, the absolute weight of pure hydrogen chloride does not undergo change, hence this factor is used in formulating the algebraic equation.

Since the specific gravity of the original reagent is 1.19, each cubic centimeter weighs 1.19 grams and the weight of the reagent is

$$50 \times 1.19 = 59.5 \text{ grams}$$

Of this weight, 37.23 per cent is pure HCl. Therefore

$$50 \times 1.19 \times 0.3723 = 22.15 \text{ grams of pure HCl}$$

The diluted reagent is to have a specific gravity of 1.10, and from the specific gravity table this is found to be a 20.01 per cent solution. This means that, in the combined weight of the original reagent and the amount of water added, there should be 20.01 per cent of hydrogen chloride. Letting x equal the weight of water to be added

$$22.15 \text{ grams} = (59.5 + x)0.2001$$

from which x equals 51.2 grams and hence 51.2 cc. of water. The foregoing steps may, of course, be combined, for ease of computation, into the equation

$$50 \times 1.19 \times 0.3723 = [(50 \times 1.19) + x] 0.2001$$

and x solved for directly.

Problems of this kind are solved on a weight basis and the equation is based on the weight of pure solute in the original and final solution. A serious error would be introduced if the calculation were made of a volume basis, because when two volumes are mixed the resulting total volume is not the sum of the separate volumes, a contraction usually taking place.

The following problem, on mixtures, will further illustrate this type of calculation.

Example 3. What will be the specific gravity of a mixture resulting from mixing 100 cc. of H_2SO_4 of specific gravity 1.40 with 100 cc. of H_2SO_4 of specific gravity 1.82?

Since the final volume will not be 200 cc. the specific gravity of the mixture cannot be calculated directly, but the percentage of H_2SO_4 in the mixture can be computed and, from the density table, the corresponding specific gravity can be found. Let x equal the percentage, by weight, of H_2SO_4 in the mixture. The problem then formulates itself thus:

$$\begin{aligned} [100 \text{ cc.} \times 1.40 \times 0.5011] + [100 \text{ cc.} \times 1.82 \times 0.9005] \\ = [(100 \times 1.40) + (100 \times 1.82)]x \\ [70.15 + 163.9] = [(140 + 182)]x \\ 234.1 = 322x \\ x = 0.7270 \text{ or } 72.70 \text{ per cent} \end{aligned}$$

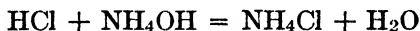
This, from the table, corresponds to a specific gravity of 1.645.

It frequently becomes necessary to calculate the volume of reagent required for a reaction. In the following problem, which concerns itself

with neutralization, the method of calculation will be illustrated for reagents of the type under consideration.

Example 4. What volume of ammonium hydroxide, specific gravity 0.970, will neutralize 10 cc. of HCl solution of specific gravity 1.12?

Reference to the density tables will show that the HCl solution contains 23.82 per cent by weight of pure HCl and that the ammonium hydroxide solution has the equivalent of 7.31 per cent NH_3 . For the chemical equation



we can write



which gives the relation, by weight, between HCl and NH_3 . The weight of HCl involved in the reaction is

$$[10 \text{ cc.} \times 1.12 \times 0.2382 = 2.668 \text{ grams.}]$$

Letting x equal the weight of NH_3 , the stoichiometric equation is

$$\frac{\text{NH}_3}{\text{HCl}} \quad \text{or} \quad \frac{17.03}{36.46} = \frac{x}{2.668}$$

whence $x = 1.246$ grams of NH_3 required.

The volume of ammonia solution is now found from the equation

$$\text{Vol.} \times 0.970 \times 0.0731 = 1.246$$

to be 17.6 cc.

5. Molar and Molal Solutions. If the molecular weight in grams, that is, the gram-molecular weight, or one gram-mole, of a solute is dissolved in water or other solvent and the solution diluted to 1000 cc., the solution is a 1-molar (or 1 *M*) solution. If the gram-molecular weight is dissolved in 1000 grams of solvent, we have what is known to the physical chemist as a 1-molal solution. Molar concentrations and the corresponding terms, gram-atom and gram-ion concentration, are the units used so extensively in equilibrium calculations. The student no doubt is familiar with calculations of this kind, from his study of the theory of qualitative analysis. In quantitative analysis the application of equilibrium theory is even more important, and frequent reference to such calculations will be made in this book at appropriate places. Molar solutions, as laboratory reagents, are not generally used in quantitative analysis, the preference being given to normal solutions, which will be discussed in the following section.

6. Normal Solutions. The designation of the strength of a solution in terms of its normality is the one most extensively used in volumetric quantitative analysis and, together with titres, is the basis of most of the

calculations in this very important branch of the subject. The normal system is based on the concept of equivalents. A gram-equivalent weight of a substance is that weight which will bring into reaction, directly or indirectly, 1 gram-atomic weight, 1.008 grams, of hydrogen. The equivalent weight, in grams, of a substance, when dissolved and made up to a liter of solution, will give a normal solution of that substance. The difference between the normal and the molar system is that, in the former the gram-equivalent weight is used, in the latter the gram-molecular weight.

Since the normality of a solution rests fundamentally on the idea of equivalents, this concept has a most important bearing in the preparation and use of solutions the strength of which is based on the normal system. Before a solution of a desired normality can be prepared it must be decided, from the chemical equation, what weight of solute constitutes a gram-equivalent weight. This will then determine the weight in grams required for the preparation of the solution. To decide what weight is equivalent to 1.008 grams of hydrogen, and hence how much substance is required for liter quantities of 1-normal (or 1 *N*) solutions, the following specific rules are applied.

Acids. For acids, the equivalent is determined by the number of replaceable hydrogens. Therefore, divide the gram-molecular weight by the number of hydrogen atoms which can be neutralized or replaced. Thus for hydrochloric acid, HCl , which contains one replaceable or ionizable hydrogen atom in the molecule, the equivalent weight is the gram-molecular weight since this amount, 36.457 grams, will furnish 1.008 grams of replaceable hydrogen. To make a liter of 1 *N* solution, therefore, there will be required 36.46 grams of pure hydrogen chloride.

Example 5. What volume of "concentrated" hydrochloric acid solution, specific gravity 1.19, should be taken for the preparation of a liter of normal solution?

Since this monobasic acid has one replaceable hydrogen, the molecular weight of the pure solute, hydrogen chloride, in grams, namely 36.46 grams, is required. The original hydrochloric-acid solution has a specific gravity of 1.19, and, referring to the density table in the Appendix, we find the percentage by weight to be 37.23. Therefore, the volume, x , of concentrated reagent necessary to furnish 36.46 grams is found by the equation

$$x \times 1.19 \times 0.3723 = 36.46$$

to be 82.30 cc. This volume then is measured out and diluted to a liter with water and the solution will be approximately a normal solution.

In acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, only one of the four hydrogen atoms is

replaceable, as is best shown by writing the formula and ionization equation in the following form:



This, then, is a monobasic acid like HCl, and the gram-equivalent is its gram-molecular weight, namely 60.0 grams. For a liter of a normal solution of this reagent, 60 grams of the pure glacial acetic acid is required, and, since the specific gravity is practically 1, 60 cc. are used.

For dibasic acids, like H_2SO_4 , one half of the gram-molecular weight is required. Oxalic acid, when used for neutralizing, likewise requires one half of the molecular weight in grams for a liter of normal solution. Phosphoric acid, for complete neutralization, contains three replaceable hydrogens, hence one-third of the gram-molecular weight is the gram-equivalent weight.

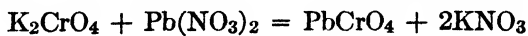
Bases. For bases, the gram-equivalent weight is calculated on the number of replaceable hydroxyl ions or their equivalent. A normal solution of a base contains, therefore, 17.008 grams of hydroxyl. For monoacid bases, like NaOH, the gram-molecular weight is directly the gram-equivalent weight, whereas, for $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$, the gram-equivalent weight is the gram-molecular weight divided by two.

Precipitating Reagents. Here the gram-equivalent weight is determined by the valence of the precipitating ion, and, to make this equivalent to one hydrogen, the rule is to divide the molecular weight by the valence of the precipitating ion of the reagent. Thus, for a normal solution of KCNS, to be employed in the precipitation of silver from AgNO_3 in the reaction:



the molecular weight of KCNS, in grams per liter, is required.

For K_2CrO_4 , in the precipitation of PbCrO_4 according to the reaction



divide the gram-molecular weight of K_2CrO_4 by 2.

Oxidizing and Reducing Agents. Here the rule is: Divide the gram-molecular weight of the reagent by the change of valence undergone by the element or ion in being reduced or oxidized. The change of valence must be determined for the reaction involved and is best arrived at, in the balancing of the equation, by finding the number of electrons gained by the oxidizing substance and lost by the reducing substance. The use of oxidizing and reducing solutions of suitable normalities constitutes such an important part of volumetric analysis that further discussion will be deferred until later.

7. Designation in Terms of Titre. The method of expressing the strength of a solution by its titre is probably the simplest and most direct of all methods. The titre of a solution is its strength in grams per cubic centimeter either of the solute contained in one cubic centimeter or the weight of substance which will react with one cubic centimeter of the solution. To illustrate: A solution which contains, say, 16.99 grams of AgNO_3 per liter would contain 0.01699 gram of AgNO_3 in 1 cc.; 0.01699 gram would be its AgNO_3 -titre. The Ag-titre of this solution would be the value of 1 cc. in terms of Ag rather than AgNO_3 contained therein and would be calculated from the relation

$$\text{Ag} : \text{AgNO}_3 = x : 0.01699$$

(107.88) (169.9)

from which $x = 0.01079$ gram, which is the Ag-titre of this solution. If one wished to know how much AgCl a certain volume of this reagent would precipitate, the appropriate titre would be the AgCl -titre, namely the grams of AgCl which would be precipitated by one cubic centimeter of this reagent. The AgCl -titre, like the Ag-titre, is found by direct proportion, or better still by the appropriate chemical factor

$$\text{AgCl} : \text{AgNO}_3 = x : 0.01699$$

or

$$\frac{\text{AgCl}}{\text{AgNO}_3} \times 0.01699 = x$$

whence

$$x = 0.01433, \text{ the AgCl-titre of this solution}$$

Frequent use is made of titres in the calculations of analytical chemistry, especially in volumetric analysis, and many illustrative examples and problems involving titres are given in this book.

PROBLEM SET 2

THE STRENGTH OF REAGENTS

✓21. What volume of KCNS solution containing 4.859 grams of KCNS per liter is required to precipitate, as AgCNS , the Ag in 0.2500 gram of AgNO_3 ?

Ans. 29.43 cc.

✓22. A gram of each of the following substances corresponds to what weight of iron: (a) FeSO_4 , (b) Fe_2O_3 , (c) $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, (d) Fe_3O_4 , (e) $\text{K}_4\text{Fe}(\text{CN})_6$?

✓23. What weight of NaOH is required to neutralize the oxalic acid liberated from the CaC_2O_4 obtained by precipitating the Ca contained in 1 gram of CaO ?

Ans. 1.426 gram.

24. Suppose (a) you add 5 grams of NaCl to 100 grams of water. What will be the percentage by weight of the NaCl in the solution? (b) If you add enough water to 5 grams of NaCl to make 100 grams of solution, what is the percentage of NaCl in the solution?

25. Calculate the weight, in grams of solute required to prepare liter quantities of (a) 1 M solutions, (b) 1 N solutions of each of the following acids:

Acid	Solute	Ans.	Molar	Normal
Hydrochloric	HCl		36.46	36.46
Nitric	HNO ₃		63.02	63.02
Sulfuric	H ₂ SO ₄		98.08	49.04
Oxalic	H ₂ C ₂ O ₄ ·2H ₂ O		126.05	63.02
Phosphoric	H ₃ PO ₄		98.04	32.68

26. A 0.1 N solution of Na₂CO₃ would contain what weight of pure Na₂CO₃ per liter?

27. What weight of NaOH, 95 per cent pure, would you take to make a liter of 0.5 N NaOH solution? Ans. 21.06.

28. What volume of water must be added to 30.0 cc. of "concentrated" HCl reagent (sp. gr. 1.19) in order to prepare a diluted reagent containing 10.17 per cent of HCl by weight?

29. In order to prepare a supply of dilute HCl of sp. gr. 1.120, how much water would you add to 150 cc. of the "concentrated" reagent which has a specific gravity of 1.190? Ans. 100.5 cc.

30. If you had need of a dilute ammonium hydroxide solution containing 5.30 per cent of NH₃ by weight, in what proportion would you mix the concentrated reagent (28.33 per cent NH₃ by weight) with water?

31. If you mix 50.00 cc. of HCl of sp. gr. 1.100 with 50.00 cc. of HCl of sp. gr. 1.170, what will be the percentage of pure HCl in the mixture? Ans. 26.94.

32. If you mix 5.00 cc. of H₂SO₄ containing 20.26 per cent of H₂SO₄ by weight with 10 cc. of H₂SO₄ containing 48.00 per cent by weight, what will be the percentage of pure H₂SO₄ in the mixture?

33. If 10.00 cc. of HCl of sp. gr. 1.20 are allowed to react with 10.00 cc. of NH₄OH of sp. gr. 0.940, will the resulting solution be acidic or ammoniacal?

Ans. Acidic.

34. What volume of ammonium hydroxide, 5.30 per cent of NH₃ by weight, is required to react with 10 cc. of dilute HNO₃ (sp. gr. 1.150)?

35. What volume of dilute hydrochloric-acid solution (sp. gr. 1.12) is required to react with 0.5000 gram of CaCO₃? Ans. 1.37 cc.

36. How many cubic centimeters of aqueous ammonia (sp. gr. 0.900, containing 28.33 per cent of NH₃ by weight) are required to precipitate the iron as Fe(OH)₃ in a sample of pure Fe₂O₃ weighing 0.5000 gram?

37. Calculate the Ag-titres (a) of a solution containing 4.859 grams of KCNS per

liter, (b) of an AgNO_3 solution containing 17 grams per liter, (c) of a solution containing 3.646 grams of HCl per liter.

Ans. (a) 0.005395; (b) 0.01080;
(c) 0.01079

✓38. A certain solution of HCl is known to contain 18.23 grams of HCl per liter. Calculate (a) the Ag -titre, (b) the NaOH -titre, (c) the Na_2CO_3 -titre, (d) the $\text{Ca}(\text{OH})_2$ -titre.

39. Calculate the molarity and the normality of the following laboratory reagents:

	<i>Ans.</i>	<i>Molarity</i>	<i>Normality</i>
(a) HCl , sp. gr. 1.12.		7.318	7.318
(b) NH_4OH , sp. gr. 0.978.		3.047	3.047
(c) H_2SO_4 , sp. gr. 1.185.		3.070	6.140

40. Calculate (a) the molarity, (b) the normality, (c) the SO_4 -titre of a solution made by dissolving 20 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in water and diluting to a liter.

PART II

THE CALCULATIONS OF VOLUMETRIC ANALYSIS

CHAPTER III

THE GENERAL CALCULATIONS OF VOLUMETRIC ANALYSIS

In principle, a volumetric determination consists of allowing the constituent being determined to react with an equivalent amount of reagent. The process, in practice, is carried out by adding an accurately measured volume of the reagent to the solution containing the constituent until an equivalent quantity has been added. The process is called titration. There must be provided some means of recognizing when the equivalent amount of reagent has been added, and this is accomplished either by use of a third substance called an indicator or else by electrical means. When the correct volume of reagent has been measured from a burette, the indicator by a sudden color change signifies the end point of the titration; or alternatively, as in a potentiometric titration, when the voltage shows a sudden rapid change, an equivalent amount of the reagent will have been added. The strength of the titrating reagent must be accurately known, and, except in a few cases, its strength is determined in a separate titration or by other means, this procedure being known as standardization.

In keeping with these general principles, an accurate method of volumetric analysis must conform to the following conditions:

1. The reaction which is selected as the basis of the determination must go practically to completion; that is, final equilibrium must be reached at the equivalent point, as indicated by the practical end point, when only a negligible amount of constituent remains untransformed.
2. The reagent used for titration must be stable and its strength must be accurately determined by a standardization process.
3. Accurately calibrated measuring apparatus, especially burettes, must be used.
4. A suitable indicator or other means of recognizing the equivalent point (the end point of the titration) must be employed.

The operations and manipulations of carrying out a volumetric

determination, with special reference to the calculations involved, may be considered to consist of two general sets of operations, namely:

- I. Preparation and standardization of reagents.
- II. Determination of the constituent in the sample.

PREPARATION OF STANDARD SOLUTIONS

In more detail, the individual steps in the preparation and standardization of the solution (or solutions) assume somewhat the following order:

1. Weighing or measuring the requisite amount of solute, and dissolving and diluting it to the proper volume; usually for student use, to one liter.
2. Weighing suitable amounts of a pure substance, known as the primary standard by which the solution is to be standardized, in case a direct primary standardization is to be made.
3. Titrating the primary standard with the solution to be standardized, noting the exact volume of reagent required for equivalence.
4. In case a second standardized solution is to be used in the determination, a comparison by titration is made between this solution and the one just standardized. Thereby the relative strength of the second reagent is established, and, by simple computation, its exact strength is calculated. This is a process of secondary standardization. Frequently, where two solutions are to be standardized, the comparison is made, in the laboratory, before either of the solutions are standardized against a primary standard.

THE DETERMINATION OF THE CONSTITUENT

With one or two standard solutions now made available, the steps in the determination of the constituent are:

5. Weighing suitable portions of the sample and properly preparing them for the analysis.
6. Titrating the dissolved samples with the standard reagent (or both reagents in case back-titration is necessary).

Coincident with these manipulative steps are the general, characteristic calculations of volumetric analysis, common to practically all determinations conducted in this manner. In addition there may be certain special computations, which, for the present, will not be considered. These general calculations will now be listed, and then described in more detail, in the same sequence as the steps upon which they are based. These calculations are:

1. Calculating the amount of solute required for the preparation of the one or more solutions to be standardized.
2. Calculating a suitable weight of primary standard.
- 3a. Calculating the strength of the solution in terms of an appropriate titre.
- 3b. Calculating the strength of the solution in terms of its normality.
4. Calculating the strength of a second solution from comparison data.
5. Calculating a suitable weight of sample for the determination.
6. Calculating the weight and percentage of constituent in the sample from titration data using (a) the titre method and (b) the normality method.

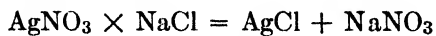
1. Calculation of the Amount of Solute for the Preparation of Solutions. In an entirely original investigation, the research chemist, in searching about for an accurate method of determination, must discover a reaction, which, when applied to the requirements of the volumetric technique, must satisfactorily fulfill the conditions specified on a previous page. Granting this has been done, the next consideration, in bringing the proposed method into workable form, is deciding upon a suitable strength of the titrating reagent, and having done so, calculating the weight of solute required for the preparation of an ample volume of reagent. What, then, constitutes a suitable strength? In practice, normalities from 0.5 to 0.01 are employed, depending upon such factors as the probable amount of constituent in the sample, the sensitiveness of the indicator and special considerations peculiar to the determination being made; in general an approximately 0.1 *N* solution is suitable in many cases.

The method of calculation of the amount of solute required for a liter quantity of solution of the desired strength depends upon the system of designating the strength. As already indicated on pages 21-24 there are in common use the titre and the normality systems.

If the titrating solution is to be used for but one kind of analysis, the titre system is the simplest. In this system, such an amount of solute is taken that each cubic centimeter of the solution will bring into reaction a specified weight of constituent. The strength of the solution should be such that a suitable volume, say between 25 and 40 cc., will be required for the titration of the constituent in the sample to be analyzed, and this in turn depends upon the amount of constituent in a given weight of sample. The chemist here is guided by a qualitative knowledge of the approximate purity of the sample and by experience and good judgment.

The calculation of the amount of solute resolves itself into a simple, stoichiometric proportion, as illustrated in the following example.

Example 1. Suppose it is desired to prepare a liter of NaCl of such strength that each cubic centimeter will bring into reaction approximately 0.005 gram of silver, when used to titrate the silver in a silver alloy according to the reaction



The amount of NaCl to be contained in 1 cc. is found from the relation

$$\begin{array}{ccc} \text{Ag} : \text{NaCl} = 0.005 : x \\ (107.9) & (58.46) & \end{array}$$

to be 0.0027 gram. Therefore, for a liter, 2.7 grams would be required.

In the normal system, the amount of solute required for a given quantity of solution of an approximate, specified normality depends upon the equivalent weight. A normal solution, as already defined on page 22, is one which contains a gram-equivalent weight of the solute in a liter of solution. The gram-equivalent weight is the weight in grams which will bring into reaction, directly or indirectly, or will correspond to, 1.008 grams of hydrogen. The equivalent weight is variously derived, depending upon the nature of the solute or the reaction in which the solution is employed. Thus, for acids, the number of equivalents in a gram-molecular weight is equal to the number of replaceable hydrogens; for bases, the number of replaceable hydroxyl; for precipitating reagents the equivalent depends on the valence of the precipitating ion and for oxidizing and reducing substances it depends upon the change of valence. To prepare liter quantities of 1 *N* solutions, that is, solutions, each of which contain a gram-equivalent weight of the solute of these several types, the following rules, already discussed in Chapter II, are observed.

1. For acids and bases, the gram-molecular weight is divided by the number of replaceable hydrogens or hydroxyls, so that a liter of solution will contain 1.008 grams of replaceable hydrogen or 17.008 grams of replaceable hydroxyl or its equivalent. This matter is further discussed and illustrated in Chapter V under the calculations of acidimetry and alkalimetry.

2. For precipitating reagents, the equivalent weight is found from the valence of the precipitating ion: hence, divide the gram-molecular weight of the solute by the *valence* of the ion which enters into the precipitating reaction. Additional discussion of normal solutions of precipitating reagents will be found in Chapter IV.

3. For oxidizing and reducing solutions of normal strength, the *change of valence* determines the equivalent weight. Normal solutions

and standard reagents of these types will be considered in detail in Chapter VI.

When the normal system is to be used, and it is in almost universal use, the approximate strength, best suited for a specific use, must be decided upon and then the proper amount of solute calculated, weighed, dissolved and made up to proper volume. Since this important feature is characteristic of practically every volumetric determination, detailed discussion will be given at appropriate places. Here, the preparation of such solutions will be illustrated for but one single simple case.

Example 2. How much NaOH should be taken for the preparation of a liter of approximately 0.3 *N* NaOH solution?

The gram-equivalent weight is the gram-molecular weight, namely 40 grams. Since a 0.3 *N* solution is required, the weight of pure NaOH is

$$0.3 \times 40 = 12 \text{ grams}$$

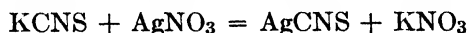
The NaOH is rarely pure and allowance must be made. If only 90 per cent pure, then the total weight is $12 \div 0.90$, or 13.3 grams for a liter of solution.

In the routine analyses in industrial laboratories it is frequently desirable to prepare a large quantity of solution, the strength of which is accurately adjusted so that each cubic centimeter of solution will represent 1 per cent, or a multiple or sub-multiple thereof, of the constituent being determined. Discussion of this type of solution will be postponed until later.

2. Calculation of the Weight of Pure Substance Required for Standardization. Having prepared a solution of the approximate required strength, its exact strength is now determined by a titration procedure. The amount of pure substance to be accurately weighed out and used in the titration is determined from the following considerations. It is assumed in the first place for the purpose of calculation that the solution to be standardized is of the exact strength desired; in the second place, the standardization is planned so that a volume of solution somewhere between 25 cc. and 40 cc. will be employed.

If, for example, the solution to be standardized is one of NaCl, to be used in the determination of silver, and was prepared by dissolving 2.7 grams of NaCl in a liter of water, each cubic centimeter will contain about 0.0027 gram of NaCl and will bring into reaction approximately 0.005 gram of silver. (See Example 1). Therefore, 0.005 gram times the volume of solution planned to be used for the standardization will represent the weight of pure silver suitable for use. For 30 cc. of solution this calls for 0.005×30 cc. or about 0.1500 gram of pure silver or its equivalent of pure silver nitrate.

Example 3. A solution of KCNS was prepared to be used in the titration of silver-alloy samples according to the reaction



and was thought to contain enough KCNS per cubic centimeter to bring into reaction approximately 0.0054 gram of silver. How much pure AgNO_3 should be used for the standardization of this solution?

If the titration is to be completed upon the addition of 35 cc., then the weight of silver involved is:

$$35 \times 0.0054 = 0.1890 \text{ gram of Ag}$$

The weight of AgNO_3 is then proportional to the weight of Ag:

$$\text{Ag} : \text{AgNO}_3 = 0.1890 : x$$

$$107.9 : 169.9 = 0.1890 : x$$

$$x = 0.2977 \text{ gram of AgNO}_3$$

If the original solution was prepared with reference to the normality system the calculation must be made on a normality basis. Suppose an approximately 0.1 *N* solution of NaCl has been prepared and is now to be standardized by allowing the solution to react with pure silver or pure AgNO_3 . The gram-equivalent weight of NaCl is its molecular weight in grams, or 58.46 grams. A liter of 0.1 *N* solution of NaCl therefore contains 5.846 grams, or each cubic centimeter contains 0.005846 gram and will react with its equivalent of Ag or AgNO_3 . The equivalent of 58.46 grams of NaCl is 169.9 grams of AgNO_3 (the molecular weight of AgNO_3 , in grams). It follows then that each cubic centimeter of 0.1 *N* NaCl will bring into reaction 0.01699 gram of AgNO_3 . If 30 cc. are to be used, a suitable weight of pure AgNO_3 would be 30 cc. times 0.01699, or 0.5097 gram.

Example 4. A solution of KCNS was prepared containing approximately 4.85 grams of KCNS per liter. This is a 0.05 *N* solution, since it contains 0.05 of 97 grams of the solute. If used for the determination of silver, as in the reaction



what weight of pure AgNO_3 should be used for its standardization?

A cubic centimeter of 0.05 *N* KCNS solution will react with a cubic centimeter of 0.05 *N* AgNO_3 solution. A liter of 0.05 *N* solution of AgNO_3 will contain 0.05 of the gram-equivalent weight, that is, 0.05×169.9 , or 8.495 grams, and 1 cc. will contain 0.008495 gram.

If 35 cc. of KCNS are to be used, there will be brought into reaction:

$$35 \times 0.008495 = 0.2973 \text{ gram of AgNO}_3$$

A suitable weight of primary standard, pure AgNO_3 , would therefore be about 0.3 of a gram.

3a. Calculation of the Strength of a Solution in Terms of Appropriate Titres. After the primary standard has been titrated by the solution to be standardized we are in possession of the necessary data by which the strength of the solution can be calculated. The data are: (1) weight of pure standard and (2) volume of solution. Dividing the weight of standard by the number of cubic centimeters required for titration obviously gives the number of grams of standard brought into reaction by 1 cc. of the solution. In other words, the strength of the reagent is now determined in terms of the substance used to standardize it and expressed as grams of standard per cubic centimeter. If, for example, we find that 30.00 cc. of a prepared KCNS solution react with 0.3000 gram of pure AgNO_3 , then

$$\frac{0.3000 \text{ gram of AgNO}_3}{30.00 \text{ cc. of KCNS}} = 0.01000 \text{ gram of AgNO}_3 \text{ per cubic centimeter of KCNS solution.}$$

This is called the AgNO_3 -titre or "value" of the KCNS solution.

If the KCNS solution is intended for use in the volumetric determination of silver, the more practical titre is the Ag-titre, i.e., the weight of pure silver brought into reaction by 1 cc. of the reagent. The Ag-titre is calculated from the AgNO_3 -titre by the simple proportion

$$\text{Ag} : \text{AgNO}_3 = x : 0.01000$$

or

$$\frac{\text{Ag}}{\text{AgNO}_3} \times 0.01000 = \text{weight of Ag per cubic centimeter}$$

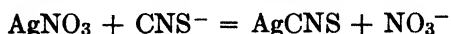
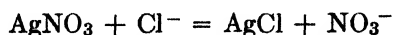
$$\frac{107.9}{169.9} \times 0.01000 = 0.006350 \text{ gram (Ag-titre)}$$

The calculation of titres is of course not limited to experimentally determined standardization data. Any desired titre for any solution can be calculated provided the strength of the solution is known in terms of any other system of units. Moreover, we can shift, at will, from one titre to other titres, if the solution is to be used for a variety of determinations. This has just been shown in the preceding illustration; another example will illustrate further how the shift is made.

Example 5. Suppose we have standardized a solution of AgNO_3 , for the purpose of a chloride determination, and found its Cl-titre to be

0.002687. We later wish to use the solution for the determination of thiocyanates. What is the CNS-titre of the AgNO_3 solution?

From the reactions



it is seen that the relation between Cl^- and CNS^- is one of direct proportion

$$\frac{\text{Cl}^-}{\text{CNS}^-} = \frac{0.002687}{x}$$

where x is the CNS^- -titre. Solving for x we find it to be 0.004395 gram per cubic centimeter.

3b. Calculation of the Strength of a Solution in Terms of Its Normality. A normal solution, by definition, is one which contains the gram-equivalent weight of solute in a liter of solution. One cubic centimeter of an exactly 1 N solution would therefore contain one-thousandth of this weight, or in other words the gram-milliequivalent weight. The normality of a solution is the ratio of the weight of solute or its equivalent in any given volume of this solution to the weight of solute or its equivalent in the same volume of a normal solution. For example, 1 cc. of a normal solution of HCl contains 0.03646 gram of HCl ; the normality of a solution of HCl which contains 0.003646 gram of HCl per cubic

centimeter would then be $\frac{0.003646}{0.03646}$, or 0.1. Moreover, if the value of

this more dilute HCl solution were expressed in its equivalent of NaOH , namely that 1 cc. is equivalent to 0.004000 gram of NaOH , then since a normal solution of NaOH contains in 1 cc. 0.04000 gram of NaOH , the normality of this HCl solution might just as well be found by the relation

$\frac{0.004000}{0.04000} = 0.1 N$, that is, the solution is 0.1 N . Or, again, if 1 cc. of the

hydrochloric acid solution were found to react with 0.005300 gram of pure Na_2CO_3 according to the reaction $\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$, its normality would be calculated by dividing the gram-milliequivalent weight of Na_2CO_3 , in this case one half of the gram-millimolecular weight, that is 0.05300 into 0.005300, and again we arrive at 0.1 as the normality of the solution.

To find the normality of a solution from experimentally determined standardization data based on a titration against a known weight of primary standard, first divide the weight of standard by the volume of reagent required; this will give the value of 1 cc. in terms of the standard

substance. Then divide this quotient by the gram-milliequivalent weight of the standard.

Example 6. Suppose that in standardizing a KCNS solution, by use of pure AgNO_3 , 0.3000 of a gram of pure AgNO_3 required 30.00 cc. of KCNS. What is the normality of the KCNS solution?

$$\frac{0.3000 \text{ gram of } \text{AgNO}_3}{30.00 \text{ cc. of KCNS}} = 0.01000 \text{ gram of } \text{AgNO}_3 \text{ per cubic centimeter of KCNS solution}$$

Since, in this reaction, the gram-equivalent weight of AgNO_3 is 169.9 or the gram-milliequivalent weight is 0.1699 we divide $\frac{0.01000}{0.1699} = 0.05886$ and find therefore that the solution is 0.05886 *N*.

In general, to find the normality of a solution, divide the weight, as expressed in grams per cubic centimeter of solute or its equivalent, by one-thousandth of the gram-equivalent weight, namely, the gram-milliequivalent weight. This will give the ratio of the value of the solution to the value of a normal solution.

4. Calculation of the Strength of a Solution from Secondary Standardization Data. Instead of standardizing a solution by titration against a weighed amount of primary standard, it is possible to standardize a solution by titration against a measured volume of a previously standardized solution. The process is known as secondary standardization. This is actually done in procedures of analysis which call for two standard solutions. The actual comparison titration, in fact, often precedes the primary standardization, and the two solutions are thus compared so that their strength relative to each other is established. To show how the calculations are carried out let us consider the following case.

Suppose that, by titration, it is found that 30.00 cc. of a hydrochloric-acid solution react with 31.00 cc. of a sodium-hydroxide solution. From the ratio, $\frac{30.00 \text{ cc. of HCl}}{31.00 \text{ cc. of NaOH}} = 0.967$ it is found that 1 cc. of NaOH is

equivalent to 0.967 cc. of HCl and, conversely, from the ratio $\frac{31.00}{30.00} =$

1.033 it is found that 1 cc. of HCl is equivalent to 1.033 cc. of NaOH solution. These ratios merely establish the relation between the two solutions, but, if the strength of one of them is known, the other can be calculated. If, for example, the strength of the hydrochloric-acid solution is known, or is later established, in terms of a titre or normality value, any desired titre or the normality of the sodium hydroxide can be found. Thus, if the Na_2CO_3 -titre of a HCl solution happens to be

0.005300, and 1 cc. of $\text{HCl} \approx 1.033$ cc. of NaOH , then the corresponding Na_2CO_3 -titre for the NaOH solution is obtained by the simple relation, $0.005300 \div 1.033$, or 0.005131.

Likewise, on a normality basis, if the HCl solution is 0.1 N , then the normality of the NaOH solution is $\frac{0.1}{1.033}$, or 0.09681.

A more direct method of computation, which, moreover, emphasizes the equivalency in the normal system, lies in the relation between the volumes and normalities of two solutions. This relationship is fundamental and can be stated thus: *The volumes of two solutions are inversely proportional to their normalities.* For example, 20 cc. of a 0.2 N solution are equivalent to 40 cc. of a 0.1 N solution. Expressed mathematically:

$$\text{or} \quad 20 \text{ cc.} : 40 \text{ cc.} = 0.1 N : 0.2 N$$

$$20 \text{ cc.} \times 0.2 N = 40 \text{ cc.} \times 0.1 N$$

Applying this fundamental relationship to the data at hand, we have

$$30.00 \text{ cc. of HCl} \times 0.1 N = 31.00 \text{ cc. of NaOH} \times x N$$

in which x is the normality of the NaOH solution, and found to be 0.09681.

Example 7. In comparing a KCNS solution with a AgNO_3 solution, it was found that 35.25 cc. of the former reacted with 36.00 cc. of the latter. Calculate the normality of the AgNO_3 solution, the KCNS solution having been found to have a normality of 0.05000.

Here we might find the ratio of the two volumes and by multiplication or division of the known normality find the normality of the AgNO_3 . Or, more simply, we might apply the volume-normality relationship:

$$\text{Vol. of KCNS} \times \text{its normality} = \text{Vol. of AgNO}_3 \times \text{its normality}$$

$$35.25 \times 0.05000 = 36.00 \times N \text{ of AgNO}_3$$

$$N = 0.04896$$

Example 8. Twenty-five cubic centimeters of a 0.5000 N solution were diluted with 25 cc. of water. What was the normality of the diluted solution?

By mere inspection, it is seen that doubling the volume reduces the normality to one half of its original value. Carrying out the computation we have

$$V_1 \times N_1 = V_2 \times N_2$$

$$25 \times 0.5000 = 50 \times N_2$$

$$N_2 = 0.2500$$

5. Calculation of the Weight of Sample. In a carefully planned procedure, the details should be so arranged that the amount of constituent in the sample reacts with a suitable volume of standard solution. This is done by adjusting the weight of the sample to the strength of the solution so that errors in measurement may be reduced to a minimum. Whenever possible, the analysis should be so arranged that the volume of standard solution required falls between the limits of 25 cc. and 40 cc. In this way, errors in burette readings are reduced, because, if, on the one hand, a very small volume of solution is used, any errors made in the reading of the burette will be magnified in the final result, and, on the other hand, if more than 50 cc. are needed, the refilling of the burette will necessitate two additional readings with the chances of more errors.

With the volume of solution fixed at some desired amount, say 35 cc., that weight of sample, then, is taken which will involve this anticipated volume. The approximate amount of the constituent in the sample should be known, but, if this information is not available, it is assumed for this calculation that the sample is pure. To illustrate the calculation, suppose that a 0.05 *N* solution of KCNS is to be used for the determination of silver in an alloy, the alloy being almost pure silver. A normal solution will involve, per cubic centimeter, the gram-milliequivalent weight of silver, namely 0.1079 gram; and a 0.05 *N* solution will involve 0.05 of this amount, i.e., 0.05×0.1079 , or 0.005395 gram of silver. Since 35 cc. are to be used, 35×0.005395 , or 0.1888 gram, is the weight of sample to use, on the assumption that the sample is pure silver. If the purity is known, approximately, the amount as calculated is divided by the supposed purity, in order to ascertain the correct weight of sample. In case the purity is not even known approximately and the titration results in too small or too large a volume, it is best to repeat the determination. The procedures in laboratory texts usually provide for a proper amount of sample.

6. Calculation of the Amount of Constituent in the Sample. We now finally arrive at the most important and crucial computation, the final objective of every quantitative analysis, namely, the amount of constituent in the sample. The weight of pure constituent, by the volumetric technique, is arrived at indirectly from the volume of standard solution used. Here, as in the preceding steps, either the titre or the normality system may be used, depending upon whether the strength of the solution is expressed in titre or in normality.

(a) *Titre Method of Computation.* If the strength of the standard solution has been calculated in terms of the appropriate titre, namely, the value of 1 cc. in terms of the constituent being determined, the calculation is an extremely simple one; in fact, a simple multiplication of

the volume used by the value of 1 cc. Thus, if each cubic centimeter of a certain solution reacts with, let us say, 0.005 gram of the constituent and 30 cc. are employed in the titration, then 30.00×0.005 , or 0.1500 gram of pure constituent, has reacted. The sample therefore contained 0.1500 gram of constituent. If the sample weighed 0.2000 gram, then the proportion of pure constituent to total weight of material is $\frac{0.1500}{0.2000}$, or 0.7500, i.e., 0.7500 of the entire sample was pure constituent. Expressed in terms of parts per hundred, that is, in percentage, we have

$$0.1500 : 0.2000 = x : 100$$

or

$$\frac{0.1500}{0.2000} \times 100 = 75.00 \text{ per cent}$$

Example 9. A certain KCNS solution was standardized and found to have a silver-titre of 0.006350. In titrating a silver-alloy sample, 32.55 cc. of KCNS solution were used. What was the weight of pure silver in the alloy?

Since each cubic centimeter brought into reaction 0.006350 gram of silver, and 32.55 cc. were required, the relationship

$$\text{Titre} \times \text{Volume} = \text{Weight of constituent}$$

applies simply,

$$0.006350 \times 32.55 = 0.2067 \text{ gram}$$

(b) *Normality Method of Computation.* Since the normal system is so universally used, it is important that this final step in calculating the results of a quantitative analysis be fully understood and mastered, in terms of the units of this system. Here a choice of two slightly different methods of calculation presents itself: We may either (1) compute the value of 1 cc. of the standard solution in terms of the constituent and multiply this value by the number of cubic centimeters used, or else (2) compute what the volume would have been had the solution been exactly 1 *N*, and then multiply this volume by the appropriate gram-milliequivalent weight. Either method, obviously, will give the weight of pure constituent which has reacted.

In method (1) the value of 1 cc. is found by multiplying the normality by the gram-milliequivalent weight of the constituent being determined. This is evident from the definition of gram-milliequivalent weight, namely the value of 1 cc. of a 1 *N* solution, so that the value of 1 cc. of a

solution, say 0.5 *N*, is 0.5 times the value of 1 cc. of a 1 *N* solution:

$$\text{Value of 1 cc.} = \text{Normality} \times \text{gram-milliequivalent weight}$$

The weight of constituent is then

$$\text{Volume used} \times \text{normality} \times \text{gram-milliequivalent weight}$$

In method (2) the recalculation of the volume of reagent used involves the fundamental relationship, already referred to on page 36, between the volumes of solution and their normalities. Volumes are inversely proportional to their normalities; for example, 30 cc. of a 0.1 *N* solution are equivalent to 3 cc. of a 1 *N* solution. If a certain titration involves 30 cc. of a 0.1 *N* solution, then, if the solution had been 1 *N*, there would be involved

$$30 \text{ cc.} \times 0.1 \text{ } N = x \text{ cc.} \times 1 \text{ } N$$

or 3 cc. of solution. If the milliequivalent weight of the constituent being determined were, let us say, 0.1079, then the weight of the constituent would be obtained by multiplying 3 cc. by 0.1079. In general

$$\begin{aligned} \text{Number of cubic centimeters of } N \text{ solution} \times \\ \text{milliequivalent weight} = \text{weight of constituent} \end{aligned}$$

Example 10. A certain KCNS solution was standardized and found to have a normality of exactly 0.05000. In titrating a silver-alloy sample, 32.55 cc. of the KCNS solution were used. What was the weight of pure silver in the alloy?

The milliequivalent weight of silver is 0.1079. Therefore the value of each cubic centimeter of solution employed is 0.05 of 0.1079,

$$0.05 \times 0.1079 = 0.005394$$

or, in terms of a formula:

$$\text{Normality} \times \text{gram-milliequivalent weight} = \text{value of 1 cc.}$$

Since 32.55 cc. were employed, the total weight of silver is

$$32.55 \times 0.005394 = 0.1756 \text{ gram}$$

Alternatively, by method (2)

$$32.55 \text{ cc.} \times 0.05 \text{ } N = 1.6275 \text{ cc. of a 1 } N \text{ solution}$$

Therefore

$$1.6275 \times 0.1079 = 0.1756 \text{ gram}$$

PROBLEM SET 3

EQUIVALENTS, NORMALITIES, TITRES

41. Calculate the gram-equivalent weight of the following substances:

(a) HCl	<i>Ans.</i> (a) 36.46 grams.
(b) Na_2CO_3	(b) 53.00 grams.
(c) H_2SO_4	(c) 49.04 grams.
(d) NH_4OH	(d) 35.05 grams.
(e) H_3PO_4	(e) 32.68 grams.

42. Calculate the gram-equivalent weight of the following precipitating reagents:

- (a) AgNO_3
- (b) KCNS
- (c) NaCl
- (d) K_2CrO_4
- (e) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

43. What are the gram-millicequivalent weights of the following substances:

(a) NaOH	<i>Ans.</i> (a) 0.04000 gram.
(b) H_2SO_4	(b) 0.04904 gram.
(c) Na_2CO_3	(c) 0.05300 gram.
(d) KCNS	(d) 0.09717 gram.
(e) NaHCO_3	(e) 0.08400 gram.

44. Calculate the titres called for below for a solution containing 3.646 grams of HCl per liter.

- (a) HCl-titre
- (b) Na_2CO_3 -titre
- (c) Cl-titre
- (d) Ag-titre
- (e) NaOH-titre

45. What are the normalities of the following solutions which contain the specified weight of solute per liter of solution?

(a) HCl containing 4.8152 grams HCl.	<i>Ans.</i> 0.1321 N.
(b) NaOH containing 4.6150 grams NaOH.	0.1154 N.
(c) H_2SO_4 containing 4.7865 grams H_2SO_4 .	0.0976 N.
(d) AgNO_3 containing 8.5000 grams AgNO_3 .	0.05003 N.
(e) NaCl containing 5.8267 grams NaCl.	0.0997 N.

46. Suppose it is desired to prepare a AgNO_3 , a KCNS and a NaCl solution, each having a Ag-titre of 0.01079. What weight of solute should be used in each case for a liter of solution?

47. Calculate the normalities of the following solutions having the specified titres.

(a) HCl having a HCl-titre of 0.003578.	<i>Ans.</i> (a) 0.0981 N.
(b) NaOH having a NaOH-titre of 0.003982.	(b) 0.0996 N.
(c) H_2SO_4 having a NaOH-titre of 0.003982.	(c) 0.0996 N.
(d) Na_2CO_3 having a HCl-titre of 0.003578.	(d) 0.0981 N.

48. The following solutions, each having a normality of 0.2685, have what titres with respect to the solute? (That is, for example what is the HCl-titre of the HCl solution?)

- (a) AgNO_3
- (b) Na_2CO_3
- (c) H_2SO_4
- (d) NaH_2PO_4
- (e) Ca(OH)_2

49. Suppose your desk reagent of hydrochloric acid has a specific gravity of 1.12 and contains 23.82 per cent of HCl by weight. How much pure HCl does each cubic centimeter contain, i.e., what is its HCl-titre? How much AgCl will a cubic centimeter of this solution precipitate? In other words, what is its AgCl-titre?

- Ans.* (a) 0.2674 gram of HCl per cc.
(b) 1.0489 gram of AgCl per cc.

50. If you have a desk reagent of NH_4OH of sp. gr. of 0.95, containing 12.74 per cent of NH_3 , what is its HCl-titre? What is its Fe(OH)_3 -titre?

51. If you desired to prepare 0.3 *N* solutions of the reagents listed below, what volumes of the concentrated reagents would you dilute for liter quantities of the required strength?

- (a) HCl, sp. gr. 1.19; 37.23 per cent HCl by weight.
- (b) H_2SO_4 , sp. gr. 1.84; 95.60 per cent H_2SO_4 by weight.
- (c) NH_4OH , sp. gr. 0.90; 28.33 per cent NH_3 by weight.

- Ans.* (a) 24.69 cc. of HCl.
(b) 8.36 cc. of H_2SO_4 .
(c) 41.26 cc. of NH_4OH .

52. A certain KCNS solution was titrated against 0.2567 gram of pure AgNO_3 , requiring 34.75 cc. Calculate the normality of the solution.

53. A certain solution was titrated against 0.2567 gram of pure AgNO_3 , requiring 34.75 cc. Calculate (a) the AgNO_3 -titre, (b) the HCl-titre, (c) the KCNS-titre, (d) the NaOH-titre of the solution.

- Ans.* (a) 0.007387 gram of AgNO_3 .
(b) 0.001585 gram of HCl.
(c) 0.004225 gram of KCNS.
(d) 0.001739 gram of NaOH.

54. How many cubic centimeters of 0.1 *N* NaOH solution will be required to neutralize 30 cc. of 0.1 *N* HCl solution? For 30 cc. of 0.5 *N* HCl? For 30 cc. of 0.5 *N* H_2SO_4 ?

55. How many cubic centimeters of a 0.05000 *N* solution of KCNS will be required to react with 30.00 cc. of a 0.5267 *N* solution of AgNO_3 ?

- Ans.* 316.02 cc. of KCNS.

56. If you add 25 cc. of water to 20 cc. of 0.1 *N* HCl, what is the normality of the resulting solution?

57. If you find by experiment that 27.65 cc. of a 0.1687 *N* solution of HCl react with 28.50 cc. of a NaOH solution, what is the normality of the latter solution?

- Ans.* 0.1637 *N*.

42 GENERAL CALCULATIONS OF VOLUMETRIC ANALYSIS

58. By titration it was found that 33.65 cc. of a HCl solution neutralized 32.00 cc. of a NaOH solution. What is the value of 1 cc. of the NaOH in terms of HCl? If the HCl has a Na_2CO_3 -titre of 0.002678, what is the Na_2CO_3 titre of the NaOH?

59. What volume of a 1 *N* solution of any solution will correspond to 25 cc. of a 0.1 *N* solution? What volume of a 1 *N* solution will 15.65 cc. of a 0.8562 *N* solution equal?

Ans. (a) 2.5 cc.

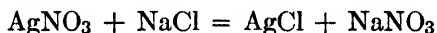
(b) 13.40 cc.

60. The gram-millicivalent weight of NaOH is 0.0400. If a reagent has a normality of 0.1682, what is the value of 1 cc. of the reagent in terms of NaOH? Distinguish, in meaning, between titre and gram-millicivalent weight as illustrated by this problem.

CHAPTER IV

CALCULATIONS OF VOLUMETRIC PRECIPITATION ANALYSIS

In order to show how the general calculations of volumetric analysis apply to the methods of volumetric precipitation and to consolidate the several steps into a complete set, it seems best to select a specific analysis. For the purpose of illustration the data obtained in the determination of chlorides by the method of Mohr will be taken as furnishing a typical example. In this method, the sample of chloride is titrated with standard AgNO_3 solution, according to the reaction



using K_2CrO_4 as the indicator. An approximately 0.1 *N* solution of AgNO_3 is found suitable and the details are managed in such a way that a convenient volume of reagent is employed, both for the standardization and the final determination. In the discussion which follows the steps will be given in the form of illustrative problems.

Example 1. How much AgNO_3 should be taken for the preparation of a liter of approximately 0.1 *N* AgNO_3 solution?

Since the valence of the precipitation ion, Ag^+ , is 1, the gram-equivalent weight is the molecular weight of AgNO_3 in grams. This is 169.9. A liter of 0.1 *N* AgNO_3 therefore calls for 16.99 grams, or approximately 17 grams.

Example 2. What weight of pure NaCl should be used to standardize a solution of AgNO_3 , thought to be about 0.1 *N*?

Assume the solution to be 0.1 *N* and that it is desired to complete the titration with 35 cc. of solution. We can here, by definite proportion, calculate the weight of NaCl required to react with 35 cc. of 0.1 *N* AgNO_3 solution. But the more logical method is to take 0.1 of the gram-milliequivalent weight of NaCl , namely $\frac{58.46}{1000} \times 0.1$, or 0.005846, and multiply this by 35.

$$\frac{58.46}{1000} \times 0.1 \times 35 = 0.205 \text{ gram}$$

A weight of NaCl of about two-tenths of a gram, accurately weighed to one-tenth of a milligram, will be suitable for this standardization.

Example 3. If, in the standardization of a AgNO_3 solution, 0.2167 gram of pure NaCl required 34.12 cc. of the solution, what is (a) the NaCl-titre and (b) the Cl-titre of the solution?

Since 0.2167 gram of NaCl reacted with 34.12 cc. of the AgNO_3 solution, 1 cc. brought into reaction $0.2167 \div 34.12$, or 0.006351 gram of NaCl. This, by definition, is the NaCl-titre of the AgNO_3 solution. The Cl-titre is then found, by direct proportion, or by use of the chemical factor, $\frac{\text{Cl}}{\text{NaCl}}$. The steps can be combined into the single equation:

$$\frac{0.2167 \times \frac{35.46}{58.46}}{34.12} = 0.003852$$

The value, 0.003852, is the Cl-titre of the AgNO_3 solution and is the weight, in grams, of chloride ion (or radical) represented by 1 cc. of the now standardized solution of silver nitrate.

Example 4. If in standardizing the silver-nitrate solution, 34.12 cc. of the solution were found to react with 0.2167 gram of NaCl, what is the normality of the solution?

Since 34.12 cc. of AgNO_3 reacted with 0.2167 gram of NaCl, 1 cc. reacted with $0.2167 \div 34.12$, or 0.006351 gram of NaCl. This means that the AgNO_3 solution is equivalent to a NaCl solution which contains 0.006351 gram of NaCl per cubic centimeter. A normal solution of NaCl contains 58.46 grams per liter, or 0.05846 gram (the gram-milliequivalent weight) of NaCl per cubic centimeter. The normality of the solution under consideration is therefore $0.006351 \div 0.05846$, or 0.1086. Combining these steps, we have:

$$\frac{0.2167}{34.12 \times 0.05846} = 0.1086 N$$

Example 5. What would be a suitable weight of sample to use, assuming the sample to be 40 per cent pure NaCl, the standard solution having a Cl-titre of 0.003852.

Let us anticipate the use of 35 cc. of the standard solution, each cubic centimeter of which will react with 0.003852 gram of chloride. This Cl-titre corresponds to a NaCl-titre of 0.006351 (see Problem 3). Then 0.006351×35 cc., or 0.2223 gram, is the weight of pure NaCl in the

impure sample. The purity is thought to be 40 per cent; therefore $0.2223 \div 0.40$, or 0.5558 gram.

$$\frac{35 \text{ cc.} \times \frac{58.46}{35.46} \times 0.003852}{0.40} = 0.5558 \text{ gram}$$

Example 6. What weight of an impure NaCl sample should be taken for analysis, if the AgNO_3 solution used for titration has a normality of 0.1086 and the sample is believed to be about 40 per cent pure NaCl?

Suppose it is planned to use about 35 cc. of the standard solution. Then the volume \times its normality \times the gram-milliequivalent weight will give the weight of pure NaCl.

$$35 \times 0.1086 \times 0.05846 = \text{weight of pure NaCl}$$

Since the sample is only about 40 per cent pure, we have

$$\frac{35 \times 0.1086 \times 0.05846}{0.40} = 0.5558 \text{ gram}$$

Example 7. If in the titration of a 0.5000-gram sample of impure NaCl, 38.65 cc. of AgNO_3 were employed, the Cl-titre of the solution being 0.003852, what is the percentage of chloride in the sample?

The total weight of chloride in the sample is obviously 38.65×0.003852 , or 0.1489 gram. Since the total weight of sample was 0.5000, the ratio is $\frac{0.1489}{0.5000}$, or 0.2978. The percentage is therefore 29.78.

$$\frac{38.65 \text{ cc.} \times 0.003852}{0.5000} \times 100 = 29.78 \text{ per cent}$$

Example 8. If in the titration of a 0.5000-gram sample of impure NaCl, 38.65 cc. of a 0.1086 *N* solution of AgNO_3 were used, what is the percentage of chloride in the sample?

The normality is 0.1086 and the gram-milliequivalent weight of Cl is 0.03546. The product of these two factors is therefore the pure Cl precipitated by 1 cc. of the solution. The total Cl, therefore, is this quantity multiplied by the volume used. We have then

$$\frac{38.65 \times 0.1086 \times 0.03546}{0.5000} \times 100 = 29.78 \text{ per cent}$$

EQUILIBRIA CALCULATIONS IN VOLUMETRIC PRECIPITATION METHODS

Reactions in aqueous solutions never run absolutely to completion, an ionic equilibrium always being established. Application of the Law of Chemical Equilibrium enables one to calculate, under given conditions, the ionic and molar concentrations of the components in a reaction. In the case of precipitation reactions, the Solubility Product Principle, one of the applications of the Law of Chemical Equilibrium, has to deal specifically with the concentration of ions which exist in a solution in which a precipitate has formed. The principle states that when equilibrium is reached in a precipitation reaction, the product of the concentrations of the ions (each concentration raised to a power corresponding to the coefficient of that particular ion as it appears in the balanced equation) is equal to a constant called the solubility product constant. For a simple case, such as the formation of AgCl, the expression takes the form

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{\text{s.p. of AgCl}}$$

in which C_{Ag^+} and C_{Cl^-} are the concentrations (gram-ion quantities in a liter) in equilibrium with solid AgCl, and $K_{\text{s.p.}}$ is the constant which, by experiment, has been found to be 1.1×10^{-10} .

In a solution containing Cl^- ions, AgCl cannot form until such a quantity of Ag^+ ions has been added that the product of the concentrations of these two ions, when referred to a liter of solution, exceeds the value 1.1×10^{-10} . Equilibrium is then first reached. This aspect of the principle, namely the appearance of a precipitate, is of considerable interest in the study of the theory of qualitative analysis, for it enables us to identify the presence of ions.

But, as more and more AgNO_3 is added, increasing amounts of AgCl are formed and the concentration of Cl^- ion steadily becomes smaller. We may ask: Is complete precipitation possible? The solubility product principle gives the answer definitely in the negative: No matter how much AgNO_3 precipitating agent is added, there will always remain some Cl^- ion, however small the concentration may eventually be. From a quantitative standpoint, then, a precipitation analysis is not absolutely perfect, and, for practical purposes, only those reactions can be used in which the amount of constituent remaining unprecipitated is so small that it cannot be measured by analytical methods.

In a volumetric precipitation analysis, an equivalent amount of standard precipitating reagent is added, at which point the titration is stopped; whereas, in a gravimetric precipitation process, an excess of reagent over the equivalent amount is purposely employed. The con-

centration of ions remaining unprecipitated, at the equivalent point, can readily be calculated from the solubility product equation; for, when an equivalent amount of reagent has been added, the ions, in equilibrium, are present in equivalent amounts, in contact with the precipitated compound. In the case of AgCl:

$$C_{Ag^+} \times C_{Cl^-} = 1.1 \times 10^{-10}$$

The equivalent quantities of Ag^+ ion and Cl^- ion are obtained by taking the square root of the K_{sp} of AgCl, i.e., $\sqrt{1.1 \times 10^{-10}}$, or approximately 1×10^{-5} gram-ion per liter each of Ag^+ and of Cl^- . This means that if one is determining chloride with standard $AgNO_3$, and conducts the titration so that the total final volume is 1000 cc., there will remain 1×10^{-5} gram-ion of chloride unprecipitated. The gram quantity of chloride remaining in solution would be 0.00001×35.46 , or approximately 0.00035 gram. This is a loss of more than 0.3 of a milligram. In a practical titration, the total final volume is usually limited to about 100 cc. so that, in this case, the loss of chloride due to incomplete precipitation would be 0.00003, an amount well beyond the experimental limit.

No matter how much AgCl is present as precipitate, the amount of Ag^+ ion and of Cl^- ion will always be the same, namely 0.00001 gram-ion of each, per liter of solution. This measures the theoretical error of the determination, that is, the error inherent in the reaction itself. The percentage error will of course depend upon the amount of AgCl precipitated.

PROBLEM SET 4

CALCULATIONS OF VOLUMETRIC PRECIPITATION ANALYSIS

61. A solution of $AgNO_3$ is known to contain 21.857 grams of $AgNO_3$ per liter. Calculate (a) the Cl-titre; (b) the Br-titre; (c) the KCN-titre; (d) the CNS-titre of this solution.

Ans. (a) 0.0045621; (b) 0.01028; (c) 0.008377; (d) 0.007471.

62. Calculate (a) the Cl-titre; (b) the Br-titre; (c) the KCN-titre; (d) the KCNS-titre of a 0.1286 *N* solution of $AgNO_3$.

63. What weight of pure, dry $AgNO_3$ should be taken for the standardization of an approximately 0.08000 *N* solution of KCNS, if not more than 40 cc. of the solution are to be used?

Ans. 0.5436 gram.

64. If in a primary standardization of a NaCl solution 35.28 cc. of the NaCl react with 0.3452 gram of pure $AgNO_3$, what is the Ag-titre and the normality of the NaCl solution?

65. If 32.75 cc. of a KCNS solution, the normality of which is 0.04782, react with 34.62 cc. of an $AgNO_3$ solution, what is the normality of the latter solution?

Ans. 0.04523 *N*.

48 CALCULATIONS OF VOLUMETRIC PRECIPITATION ANALYSIS

66. A sample of common table salt was titrated with standard AgNO_3 solution, requiring 42.60 cc. of the solution, whose normality was 0.1067. The weight of sample was 0.2733 gram. Calculate the percentage purity of the NaCl .

67. What weight of KCNS will be required to react with 0.2576 gram of AgNO_3 ? If this weight of KCNS is contained in 35.00 cc. of solution, what is the value of 1 cc. of the KCNS solution (a) in terms of KCNS (the KCNS -titre); (b) in terms of AgNO_3 (the AgNO_3 -titre); (c) in terms of Ag (the Ag -titre)?

Ans. 0.1473 gram; (a) 0.004209; (b) 0.007360; (c) 0.004674.

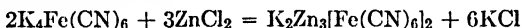
68. A sample of silver was titrated, using 20.50 cc. of a 0.1273 N solution of NaCl and 1.65 cc. of a 0.01000 N solution of NaCl . Calculate the weight of silver in the sample.

69. If, in the analysis of a sample of silver alloy by titration with KCNS , it was found that 35.65 cc. of the standard solution, each cubic centimeter of which was equivalent to 0.005 gram of Ag , were required to react with the silver in 0.2386 gram of the sample, what is the percentage of silver in the sample?

Ans. 74.73 per cent.

70. A sample of soluble chloride was titrated by a solution of AgNO_3 containing 8.4945 grams of the solute in 500 cc. The volume required for the titration was 28.75 cc. Calculate the weight of chloride precipitated using (a) the Cl -titre; (b) the normality of the standard solution.

71. According to the reaction



used in the volumetric determination of zinc, calculate the weight of $\text{K}_4\text{Fe}(\text{CN})_6$ required for the preparation of a liter of 0.1 N solution. *Ans.* 12.276 grams.

72. It is desirable that the volumes of 0.05 N solution of NaCl (Ag -titre = 0.005395) used for titrating samples of silver alloy should range between 25 cc. and 50 cc. What weights of alloy should be taken for analysis if the samples are thought to contain approximately (a) 1 per cent; (b) 10 per cent; (c) 40 per cent; (d) 60 per cent; (e) 95 per cent, of silver?

73. What percentage error is involved in the determination of a sample of chloride if, after titration with AgNO_3 , the final total volume is 150 cc.? The $K_{s.p.}$ of AgCl is 1×10^{-10} , and the sample is known to contain 0.1267 gram of chloride.

Ans. 0.042 per cent.

74. If after titrating the silver in a sample of alloy with KCNS solution, the final volume of titrated solution is 200 cc., what gram weight of silver remains unprecipitated? The $K_{s.p.}$ of AgCNS is 7.1×10^{-13} . If the percentage of silver in the alloy is 90.00, what error is involved in this loss?

75. Four samples of silver alloy, containing, respectively, 25.00, 50.00, 75.00 and 100 per cent of silver, are given to four students for analysis. They report percentages of silver as follows: 24.95, 49.95, 74.95 and 99.95. Calculate (a) the error in percentage; (b) the deviation in parts per thousand from the correct result; (c) the percentage error.

<i>Ans.</i>	(a)	0.05	0.05	0.05	0.05.
	(b)	2	1	0.67	0.5.
	(c)	0.2	0.1	0.067	0.05.

76. The nickel content of ores and salts may be determined by titrating the ammoniacal sample with standard KCN solution, the first reaction taking place being the precipitation of nickel cyanide.



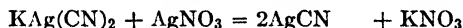
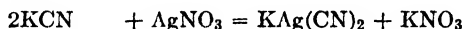
The $\text{Ni}(\text{CN})_2$ dissolves in an excess of KCN forming a nickel-cyanide complex ion:



What is the gram-equivalent weight of KCN for this set of reactions?

77. How many grams of K_2CrO_4 must be taken to make a liter of 0.1 *N* solution to be used for the precipitation of lead as PbCrO_4 ? What is the Pb-titre of a 0.5213 *N* solution of K_2CrO_4 ? *Ans.* 9.711 grams; 0.05401.

78. Soluble cyanides can be determined by volumetric precipitation with standard silver nitrate, the end point being recognized by the precipitation of AgCN . The reactions involved are:



If, in such an analysis, a given weight of sample required 30.00 cc. AgNO_3 solution whose Ag-titre was 0.0050, what weight of KCN was present?

79. A 0.6324-gram sample of material containing iodides was analyzed for its iodide content by treating a solution of the sample with 50.00 cc. of 0.1 *N* AgNO_3 , filtering off the precipitated AgI , and titrating the excess AgNO_3 with 20.00 cc. of 0.05 *N* KCNS. Calculate the percentage of iodide present.

Ans. 80.28 per cent.

80. A student weighs 2.5000 grams of a sample of a chloride, dilutes to 500 cc., and uses a portion of this solution for a chloride determination. The sample was found to contain 25.00 per cent of chloride. What was the gram-ion concentration of chloride?

CHAPTER V

THE CALCULATIONS OF NEUTRALIZATION ANALYSIS

Neutralization reactions are utilized in volumetric analysis to determine the neutralizing ability of acids and bases and of salts which have acidic or basic properties. The available acidity or basicity of such compounds is determined by titration with standardized solutions of bases and acids. As with volumetric precipitation procedures, the same general requirements and conditions must here be met, namely (1) the reaction must be substantially complete, (2) the standard solutions employed must be stable and (3) the equivalence point must be capable of being recognized by a chemical indicator or by electrical means. With respect to the recognition of the end point, either organic dye-stuff indicators are used which show a sudden color change at the equivalence point or, alternatively, the titration may be conducted potentiometrically, by which technique the end point can also be found. The standard solutions are usually hydrochloric acid and sodium hydroxide, of a strength ranging between 0.5 *N* and 0.1 *N*.

For the purpose of study and discussion the calculations of neutralization procedures will be taken up in the following order.

- A. The use of standard solutions of acids and bases (Problem Set 5).
- B. The theory of neutralization titrations; equilibrium and indicator theory (Problem Set 6).
- C. The adjustment of solutions; mixed alkali titrations; additional applications (Problem Set 7).

A. THE USE OF STANDARD SOLUTIONS OF ACIDS AND BASES

The operations and the calculations incident to the procedures of volumetric analysis have already been discussed and illustrated in a general way, as well as specifically applied to a typical volumetric precipitation procedure. Illustrative problems will now be presented to show how such calculations are involved in a typical neutralization procedure. For this purpose the determination of the available alkalinity of soda ash (impure Na_2CO_3) has been selected. The procedure, in brief, involves the preparation, comparison and standardization of solutions of

HCl and NaOH, and by use of these two solutions a suitable weight of the soda ash sample is titrated. The illustrative problems are arranged in the following sequence of examples.

In Example 1 the preparation of an approximately 0.1 *N* solution of HCl is shown. Example 2 illustrates the preparation of a solution of NaOH of approximately the same strength. Comparison data are presented in Example 3. Data for the standardization of the HCl solution are involved in Examples 4, 5 and 6. Using the data of Example 3 and the strength of the HCl we make the calculation of the strength of the NaOH, as illustrated by Examples 7 and 8. A weight of a soda-ash sample suitable for analysis is calculated, according to Example 9. Calculation of the percentage of Na_2CO_3 in a sample of soda ash made according to the titre method is presented in Example 10, and in Example 11 the calculation of the percentage is based on the normality.

Example 1. What volume of concentrated hydrochloric acid solution, specific gravity 1.19, containing 37.23 per cent of pure hydrogen chloride should be used for the preparation of a liter of approximately 0.1 *N* HCl solution?

A normal solution of any acid contains the gram-equivalent weight of replaceable hydrogen, namely 1.008 grams per liter. For a monobasic acid, such as HCl, this quantity is furnished by a gram-molecular weight of the solute. A 0.1 *N* solution of HCl must therefore contain one-tenth of the molecular weight, or 3.646 grams of solute. The source of this as given in the above example, is concentrated hydrochloric acid of specific gravity 1.19, which, from the specific-gravity table in the Appendix, corresponds to 37.23 per cent of pure hydrogen chloride. The volume of this reagent required can now be readily calculated.

$$x \text{ cc.} \times 1.19 \times 0.3723 = 3.646 \text{ grams of pure solute}$$

Therefore

$$x = \frac{3.646}{1.19 \times 0.3723} = 8.23 \text{ cc. of concentrated HCl required for a liter of 0.1 } N \text{ HCl solution}$$

Example 2. What weight of NaOH, 90 per cent pure, should be dissolved and diluted to a liter for the preparation of a 0.1 *N* solution?

A normal solution of a base should contain 17.008 grams of replaceable hydroxyl per liter. For NaOH this calls for 40.008 grams of the pure solute, and for a 0.1 *N* solution approximately 4 grams. Since the reagent is about 90 per cent pure, the weight required is

$$4.00 \div 0.90 = 4.44 \text{ grams}$$

Example 3. In comparing the strength of an approximately 0.1 *N* HCl solution with that of a NaOH solution, the following data, for three titrations, were obtained:

(a) 30.25 cc. of HCl required 28.03 cc. of NaOH.

(b) 37.60 cc. of HCl required 34.79 cc. of NaOH.

(c) 42.55 cc. of HCl required 39.42 cc. of NaOH.

Calculate the volume of HCl equivalent to 1 cc. of NaOH and, conversely, the volume of NaOH equivalent to 1 cc. of HCl.

Since in (a) 30.25 cc. of HCl \approx 28.03 cc. of NaOH we have for (a)

$$1 \text{ cc. of HCl} = \frac{28.03}{30.25} = 0.927 \text{ cc. of NaOH}$$

for (b)

$$1 \text{ cc. of HCl} = \frac{34.79}{37.60} = 0.925 \text{ cc. of NaOH}$$

and for (c)

$$1 \text{ cc. of HCl} = \frac{39.42}{42.55} = 0.926 \text{ cc. of NaOH}$$

Average 1 cc. of HCl \approx 0.926 cc. of NaOH.

Likewise, since in (a) 28.03 cc. of NaOH \approx 30.25 cc. of HCl for (a)

$$1 \text{ cc. of NaOH} = \frac{30.25}{28.03} = 1.079 \text{ cc. of HCl}$$

for (b)

$$1 \text{ cc. of NaOH} = \frac{37.60}{34.79} = 1.081 \text{ cc. of HCl}$$

for (c)

$$1 \text{ cc. of NaOH} = \frac{42.55}{39.42} = 1.079 \text{ cc. of HCl}$$

Average

$$1 \text{ cc. of NaOH} \approx 1.080 \text{ cc. of HCl}$$

Example 4. How much pure Na_2CO_3 should be used for the standardization of the HCl solution prepared in Example 1, namely, an approximately 0.1 *N* solution?

Here, for the purpose of calculation, let us assume the HCl solution to be 0.1 *N* and anticipate using a volume of 35 cc. From the reaction:



it is seen that the gram-equivalent weight of Na_2CO_3 is one half of the gram-molecular weight since two equivalents of HCl are needed for neutralization. Since the molecular weight of Na_2CO_3 is 106, the milliequivalent weight is therefore 0.053. Therefore 1 cc. of 0.1 N HCl will bring into reaction 0.0053 gram of Na_2CO_3 and, therefore,

$$0.1 \times 0.053 \times 35 = 0.1855 \text{ gram of } \text{Na}_2\text{CO}_3$$

Example 5. In standardizing an approximately 0.1 N solution of HCl against pure Na_2CO_3 , the following data were secured:

	Weight Na_2CO_3	cc. HCl	cc. NaOH
(a)	0.2152	37.82	2.64
(b)	0.2105	37.67	3.26
(c)	0.2094	36.16	1.92

Calculate the strength of the HCl solution, in terms of the Na_2CO_3 -titre.

The net volume of HCl used for the neutralization of the Na_2CO_3 must first be found. Since 1 cc. of NaOH is equivalent to 1.080 cc. of HCl , according to the data of Example 3, the net volumes of HCl , for the three titrations, are

$$(a) \quad 37.82 - (2.64 \times 1.080) = 34.97 \text{ cc.}$$

$$(b) \quad 37.67 - (3.26 \times 1.080) = 34.15 \text{ cc.}$$

$$(c) \quad 36.16 - (1.92 \times 1.080) = 34.09 \text{ cc.}$$

Then, since the Na_2CO_3 -titre is defined as the weight of Na_2CO_3 neutralized by 1 cc. of HCl , we have,

$$(a) \quad \frac{0.2152 \text{ gram}}{34.97 \text{ cc.}} = 0.006154 \text{ gram per cubic centimeter}$$

$$(b) \quad \frac{0.2105 \text{ gram}}{34.15 \text{ cc.}} = 0.006164 \text{ gram per cubic centimeter}$$

$$(c) \quad \frac{0.2094 \text{ gram}}{34.09 \text{ cc.}} = 0.006143 \text{ gram per cubic centimeter}$$

The average Na_2CO_3 -titre of the HCl solution is therefore the mean of these three values, namely 0.006154 gram.

Example 6. Calculate the normality of an approximately 0.1 N solution of HCl , using the data given in Example 5.

In Example 5, the average weight of Na_2CO_3 neutralized by 1 cc. of the HCl solution has been found to be 0.006154 gram. The problem then

resolves itself into finding the normality of a Na_2CO_3 solution, each cubic centimeter of which contains 0.006154 gram of Na_2CO_3 . Since an exactly normal solution of Na_2CO_3 contains in a liter 53.00 grams, or 1 cc. contains the gram-milliequivalent weight, that is, 0.05300 gram, the normality is $\frac{0.006154}{0.05300}$, or 0.11611. That is, the solution is 0.11611 *N*.

Example 7. Using the data of Examples 3 and 5, calculate the strength of the NaOH solution in terms of its Na_2CO_3 -titre. This problem might be expressed thus: Find the strength of a NaOH solution, in terms of its Na_2CO_3 -titre, 1 cc. of which is equivalent to 1.080 cc. of an HCl solution, whose Na_2CO_3 -titre is 0.006154.

The comparison data of Example 3 show that 1 cc. of NaOH is equivalent to 1.0080 cc. of HCl and each cubic centimeter of the HCl solution, according to the calculation of Example 5, reacted with 0.006154 gram of Na_2CO_3 . Hence, Na_2CO_3 -titre of the NaOH solution is 1.080×0.006154 , or 0.006646 gram.

Example 8. Using the data of Examples 3 and 7, calculate the normality of the NaOH solution. In other words, find the normality of a NaOH solution, 1 cc. of which is equivalent to 1.08 cc. of a 0.1161 *N* solution of HCl .

The Na_2CO_3 -titre of the NaOH has been calculated, in Example 7, based on the data of Examples 3 and 5, and found to be 0.006646 gram of Na_2CO_3 per cubic centimeter of NaOH . The normality of the NaOH solution is therefore

$$\frac{0.006646}{0.0530} = 0.1254$$

Example 9. What weights of soda ash would be required for analysis, assuming a 90 per cent sample, if the net volume of HCl is to fall between the limits of 25 cc. and 40 cc., and the Na_2CO_3 -titre of the HCl is 0.006154?

Since each unit volume will bring into reaction 0.006154 gram of Na_2CO_3 , as a minimum weight we would have

$$\frac{25 \text{ cc.} \times 0.006154}{0.90} = 0.1710 \text{ gram}$$

and, as a maximum, using 40 cc., the weight would be

$$\frac{40 \text{ cc.} \times 0.006154}{0.90} = 0.2736 \text{ gram}$$

Example 10. Calculate the total alkalinity, in terms of percentage of Na_2CO_3 , of a sample of soda ash based on the following data, using the titre method of calculation. The strength of the HCl is expressed as 0.006154 gram of Na_2CO_3 , and 1 cc. of NaOH = 1.080 cc. of HCl .

	Weight Sample	Vol. HCl	Vol. NaOH
(a)	0.2135 gram	32.62 cc.	1.42 cc.
(b)	0.2218 gram	35.25 cc.	2.75 cc.
(c)	0.2208 gram	34.86 cc.	2.48 cc.

The net volumes of HCl used are

$$(a) \quad 32.62 - (1.42 \times 1.080) = 31.09 \text{ cc.}$$

$$(b) \quad 35.25 - (2.75 \times 1.080) = 32.28 \text{ cc.}$$

$$(c) \quad 34.86 - (2.48 \times 1.080) = 32.18 \text{ cc.}$$

The percentages of Na_2CO_3 are then

$$(a) \quad \frac{31.09 \times 0.006154}{0.2135} \times 100 = 89.60$$

$$(b) \quad \frac{32.28 \times 0.006154}{0.2218} \times 100 = 89.56$$

$$(c) \quad \frac{32.18 \times 0.006154}{0.2208} \times 100 = 89.69$$

Example 11. Calculate the total alkalinity, in terms of the percentage of Na_2CO_3 , of the soda-ash sample based on the data of Problem 10, using the normality method. The standard solution of HCl is 0.11611 N , and 1 cc. of NaOH = 1.080 cc. of HCl .

Since the normality of the HCl is 0.11611 and the milliequivalent weight of Na_2CO_3 is 0.0530, each cubic centimeter of the acid will bring into reaction (0.11611×0.0530) gram of Na_2CO_3 . The net volume of HCl used in the first run is $32.62 - (1.42 \times 1.080)$, or 31.080 cc.

Therefore

for (a)

$$\frac{31.08 \times 0.1161 \times 0.0530}{0.2135} \times 100 = 89.60 \text{ per cent}$$

for (b)

$$\frac{32.27 \times 0.1161 \times 0.0530}{0.2218} \times 100 = 89.56 \text{ per cent}$$

for (c)

$$\frac{32.18 \times 0.1161 \times 0.0530}{0.2208} \times 100 = 89.69$$

The foregoing examples represent a complete set of stoichiometric calculations such as are involved in a typical alkalimetric or acidimetric determination. In actual practice and in routine work, certain steps can be eliminated and others shortened. Thus, in the first place, it must be decided in advance whether the strengths of the titrating solutions are to be designated in terms of titre or normality, and whichever basis is employed, the calculations are based on the selected system and all calculations involving the rejected system are naturally omitted. The titre system is perhaps simpler and involves a direct-weight relationship, but the normal system is more comprehensive and is to be preferred not only because, in practical work, the same standard solutions might be used for a variety of determinations without recalculation of strength designation but chiefly because the normal system emphasizes the concept of equivalency in chemical reactions.

In the second place, once the titrating solutions have been prepared and standardized, further calculations involving such preparation and standardization need not be duplicated. There remain then only the calculations based on the titration of the sample.

The following problem set (No. 5) includes calculations encountered in the preparation, standardization and use of various acids and bases. Additional problems of a more complicated nature will be found in problem set No. 7.

PROBLEM SET 5

SIMPLE CALCULATIONS OF ACIDIMETRY AND ALKALIMETRY

81. What weight of pure CaO should be taken for the preparation of 1 liter of a 0.2 N solution of $\text{Ca}(\text{OH})_2$? *Ans.* 5.608 grams.

82. If you had need for 500 cc. of a 0.1 N solution of H_2SO_4 , what volume of the concentrated sulfuric acid (sp. gr. 1.840; 95.60 per cent H_2SO_4 by weight) would you dilute?

83. To prepare 2 liters of 0.1 N solution of HCl , what volume of the reagent which contains 37.23 per cent of pure HCl and has a specific gravity of 1.19 would be required? *Ans.* 16.46 cc.

84. In order to make a liter of 0.05 N solution of NH_4OH , what volume of concentrated ammonium hydroxide, sp. gr. 0.900 and containing 28.33 per cent of NH_3 by weight, would be required?

85. What volume of "concentrated" reagent should be taken to prepare a liter of 0.1 N solution of each of the following acids: (a) HCl (sp. gr. 1.19; 37.23 per cent HCl by weight); (b) HNO_3 (sp. gr. 1.420; 69.77 per cent HNO_3 by weight); (c) H_2SO_4 , sp. gr. 1.840; 95.60 per cent by weight?

Ans. (a) 8.23 cc.; (b) 6.36 cc.; (c) 2.78 cc.

86. Calculate the Na_2CO_3 -titre for each of the following solutions: (a) 0.5123 N HCl ; (b) 0.4962 N NaOH ; (c) 30 cc. of a solution containing 0.2500 gram of Na_2CO_3 .

87. What are the titres, in terms of solute, for each of the following 0.1 *N* solutions of acids and bases: (a) HCl; (b) Na_2CO_3 ; (c) NH_4OH ; (d) $\text{H}_2\text{C}_2\text{O}_4$?

Ans. (a) 0.003646; (b) 0.005300; (c) 0.003505; (d) 0.004501.

88. In standardizing a H_2SO_4 solution, 0.2500 gram of pure Na_2CO_3 was employed. It required 37.50 cc. of the acid. What was the normality of the acid?

89. What weight of pure, dry Na_2CO_3 should be used in the standardization of an approximately 0.5 *N* solution of HCl, if not more than 30.00 cc. of the acid is to be used?

Ans. 0.7950 gram.

90. If 25.00 cc. of an exactly 0.1 *N* solution of HCl are neutralized by 26.50 cc. of a NaOH solution, what is the normality of the latter solution?

91. Upon titrating a solution of NaOH with HCl it was found that 30.25 cc. of the former reacted with 31.70 cc. of the latter. Subsequent standardization of the HCl solution showed it to be 0.1376 *N*. Calculate the normality of the NaOH solution.

Ans. 0.1442 *N*.

92. A solution was made by dissolving 6.80 grams of NaOH, 560 grams of KOH and 12 grams of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 1 liter of water. What are (a) the HCl-titre and (b) the normality of the resulting solution?

93. A certain weight of Na_2CO_3 required 32.71 cc. of HCl (1 cc. = 0.05261 gram of Na_2CO_3) and 2.10 cc. of NaOH (1 cc. of NaOH = 1.15 cc. of HCl). What weight of pure Na_2CO_3 was present in the sample?

Ans. 1.593 grams.

94. In the Kjeldahl method for the analysis of ammonium salts, the NH_3 is displaced by strong NaOH and absorbed in an excess of standard acid and the excess titrated with standard alkali. If the NH_3 from a 1-gram sample is absorbed in 50.00 cc. of 0.1 *N* HCl and the excess titrated with 3.61 cc. of 0.05 *N* NaOH, what is the percentage of NH_3 ?

95. A student prepared a dilute ammonium-hydroxide solution of sp. gr. 0.994 by dilution of the concentrated reagent, and then titrated 25 cc. of this diluted reagent with 0.5 *N* HCl, using 40.00 cc. What is the percentage by weight of NH_3 in the sample?

Ans. 1.37 per cent.

96. A 1.0000-gram sample of soda ash was titrated with 42.60 cc. of HCl, 1 cc. of which is equivalent to 1.38 cc. of NaOH. For back-titration 3.52 cc. of NaOH were used. The Na_2CO_3 -titre of the HCl was 0.02112. What was the percentage of Na_2CO_3 in the sample?

97. Suppose you had a desk reagent of dilute HCl (sp. gr. 1.12) and wished to determine the content of pure HCl. To do this, you might take 25 cc. of the reagent, dilute it to 500 cc. in a volumetric flask and, withdrawing 25 cc. of this diluted sample, titrate this with standard NaOH. If 45.73 cc. of 0.2 *N* NaOH are used, what is the percentage of pure HCl in the original reagent?

Ans. 23.82 per cent.

98. What is the percentage of CaO in a limestone sample, if 0.5000 gram required 32.75 cc. of 0.5 *N* H_2SO_4 for neutralization?

99. A 1-gram sample of a substance containing sodium carbonate was titrated with 30.00 cc. of HCl, 1 cc. of which contained 0.003562 gram of HCl. For back-titration there were required 1.27 cc. of a 0.1250 *N* NaOH solution. What was the percentage of Na_2CO_3 ?

Ans. 14.69 per cent.

100. Calculate the percentage of $\text{H}_2\text{C}_2\text{O}_4$ in a sample of crystallized oxalic acid which weighed 0.1750 gram and required 27.20 cc. of NaOH , and 2.60 cc. of HCl (1 cc. of $\text{NaOH} \approx 1.1$ cc. of HCl ; 1 cc. of $\text{HCl} = 0.002600$ gram of Na_2CO_3).

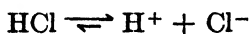
B. THE THEORY OF NEUTRALIZATION TITRATIONS: EQUILIBRIUM CALCULATIONS; CALCULATION OF HYDROGEN-ION CONCENTRATIONS AND pH VALUES; CALCULATION OF TITRATION CURVES

The theory of ionization states that when substances such as inorganic acids, bases and salts are placed in a solvent like water, the molecules of the solute dissociate more or less completely into their respective ions. Solutes which dissociate practically completely are called strong electrolytes, those in which the proportion of ions to non-ionized molecules is small, in comparable solutions, are weak electrolytes. Non-electrolytes are those which do not dissociate. The degree of ionization, usually expressed as a percentage for a number of acids, bases and salts is given in Table X in the Appendix. Particular attention is called to the strongly ionized acids such as HCl and HNO_3 as compared to weak ones such as $\text{HC}_2\text{H}_3\text{O}_2$, H_2S and HCN . In like manner NaOH is a typically strong base whereas NH_4OH is a weakly ionized one. Most salts show a fairly high degree of ionization, those of the uni-uni type as NaCl , NH_4NO_3 and $\text{NaC}_2\text{H}_3\text{O}_2$ being ionized 80 per cent or more, in 0.1 N solutions.

The extent or degree of ionization, usually expressed as a percentage of the total solute present, is determined experimentally by electrical conductivity or other physicochemical methods. The concentration of the ions in a solution can then be readily calculated if we know the degree of ionization and the total amount of solute present.

Example 1. What is the hydrogen-ion concentration in a 0.1 N solution of HCl (identical with a 0.1 M solution, since for monobasic acids the gram-equivalent weight is also the gram-molecular weight), the ionization taking place to the extent of 94.8 per cent?

The dissociation of the solute into its ions takes place according to the equation



Since the solution contains 0.1 of a gram-mole of HCl per liter and 94.8 per cent of this is ionized, the H^+ -ion concentration is

$$0.1 \times 0.948 = 0.0948 \quad \text{or} \quad 9.48 \times 10^{-2}$$

In a solution of any electrolyte, the ions and non-ionized portions of the solute are always in equilibrium, so that there is a definite ratio between the concentrations of ions and non-ionized molecules. This ratio varies considerably for a strong electrolyte such as HCl for various

normalities (or molarities) but *for weak electrolytes, such as $\text{HC}_2\text{H}_3\text{O}_2$ and NH_4OH , the ratio is always constant.* This constant ratio is known as the *ionization constant*. For acetic acid, the equilibrium relationship is expressed by the formula

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K_{(\text{ion})} = 1.8 \times 10^{-5}$$

where C_{H^+} and $C_{\text{C}_2\text{H}_3\text{O}_2^-}$ are the concentrations, in gram-ion quantities per liter, $C_{\text{HC}_2\text{H}_3\text{O}_2}$ is the concentration of non-ionized acetic acid and $K_{(\text{ion})}$ is the ionization constant for this weak acid, and has an average value of 1.8×10^{-5} . To ascertain whether a given electrolyte has an ionization constant, the equilibrium ratios are calculated for a number of different molarities and, if these ratios are substantially constant, the electrolyte is said to possess an ionization constant. Such constants for a number of weak acids and for NH_4OH are given in Table XI in the Appendix. The following example shows how the ratio is calculated for one particular molarity of NH_4OH .

Example 2. Calculate the value of K_{ion} for a 0.1 *N* (or molar) solution of NH_4OH .

The ionization takes place according to the reaction



for which the equilibrium formula holds

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = K_{(\text{ion})}$$

A 0.1 *N* solution of NH_4OH is 1.31 per cent ionized.

Therefore

$$\frac{0.1 \times 0.0131 \times 0.1 \times 0.0131}{0.1 \times 0.9869} = 1.75 \times 10^{-5}$$

The value as calculated for a 0.1 *N* solution is therefore 1.75×10^{-5} .

Equilibrium of the Ions of Water. Water, too, behaves as a very weak electrolyte, dissociating to a slight extent into hydrogen and hydroxyl ions, according to the reaction



The ionization constant of water is expressed by the equation

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{HOH}}} = K_{(\text{ion})}$$

Since, however, the total molar concentration of water remains practically unchanged owing to its feeble ionization, the equilibrium formula may be simplified by rewriting it in the form:

$$C_{H^+} \times C_{OH^-} = K_{(ion)} \times C_{HOH} = K_w$$

where K_w is a modified ionization constant and is known as the "water constant." The numerical value of K_w , determined by several independent, experimental methods, is 1.2×10^{-14} at 25° C. It is sometimes convenient to rewrite the equation

$$C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$$

in the form

$$C_{H^+} \times C_{OH^-} = 1 \times 10^{-13.92}$$

and, as an approximation, for less exact calculations we may use simply 1×10^{-14} , or merely 10^{-14} .

This relationship is of fundamental importance in the study of all aqueous solutions, especially in all neutralization reactions, for it shows that, no matter whether an aqueous solution of an acid, a base or a salt, or pure water itself, is under consideration, the product of the gram-ion concentrations of H^+ and OH^- is always constant and, at 25° C., has the value 1.2×10^{-14} .

We define an acidic solution as one having an excess of hydrogen ions, namely one in which the H^+ -ion concentration exceeds 10^{-7} and in which the OH^- -ion concentration at the same time is less than 10^{-7} . Conversely, a basic solution is one having an OH^- -ion concentration greater than 10^{-7} together with a H^+ -ion content less than 10^{-7} . A neutral solution, as well as pure water itself, contains equal concentrations of both H^+ and OH^- , namely 10^{-7} gram-ion of each per liter. As a necessary consequence of this important relationship of the water equilibrium, it follows that no matter what type of aqueous solution is referred to, the value $C_{H^+} \times C_{OH^-} = K_w = 1.2 \times 10^{-14}$ must be satisfied and that, if the value of one set of ions, either hydrogen or hydroxyl, is known or measured the concentration of the other is readily calculated. It is sufficient to designate merely one set of ions, either the hydrogen or the hydroxyl concentration in order to indicate the character or nature of the solution. Thus, a solution which is known to have a hydrogen-ion concentration of, let us say, 10^{-5} must have a corresponding hydroxyl-ion concentration of 10^{-9} ; or, again, one in which the OH^- -ion concentration is 10^{-4} must, by virtue of the water equilibrium, have a H^+ -ion concentration of 10^{-10} .

It has become customary to employ the H^+ -ion concentration, instead of the hydroxyl, as an index in designating the nature of a solu-

tion with respect to its acidity or basicity. This is due chiefly to the fact that the hydrogen-ion concentration can be measured directly. This experimental determination of the hydrogen-ion concentration of a solution is usually carried out electrically, by means of a potentiometer and standard electrodes, as described later. The value, thus obtained, may then be expressed in decimal form, in exponential form, or in terms of what is known as the "*pH* value."

Measurement and Calculation of *pH* Values. The meaning of *pH* can best be understood by considering the potentiometric method of measuring H^+ -ion concentrations. This consists, briefly, in measuring the electromotive force (voltage) set up in an electrolytic cell between a standard ("normal") hydrogen electrode (a platinum electrode coated with platinum black and saturated with hydrogen gas) which dips into a HCl solution whose H^+ -ion concentration is exactly 1 (normal with respect to H^+ ions) and another hydrogen electrode which dips into the solution whose H^+ -ion concentration is to be measured. The electrodes are connected externally to a potentiometer and internally by means of a U-tube filled with a conducting solution such as KCl . The electrons which flow from one electrode to the other through the external circuit are measured, as voltages (E.M.F.), on the potentiometer. The formula, a modification of the Nernst equation, which relates the voltage of the cell to the hydrogen-ion concentration, is:

$$E.M.F. = 0.059 \log \frac{1}{C_{H^+}}$$

in which 0.059 is a constant, "1" is the concentration of H^+ -ions in the standard or reference (normal) half-cell and C_{H^+} is the hydrogen-ion concentration in the other half-cell into which the second hydrogen electrode dips. In practice, a standard calomel electrode is frequently used instead of the standard hydrogen electrode.

By measuring the E.M.F. the factor, $\log \frac{1}{C_{H^+}}$ can be calculated:

$$\frac{E.M.F.}{0.059} = \log \frac{1}{C_{H^+}}$$

and from this, the value of C_{H^+} can be obtained. But, instead of solving for C_{H^+} directly, the symbol, *pH*, has been introduced to represent \log

$\frac{1}{C_{H^+}}$, i.e.,

$$\log \frac{1}{C_{H^+}} = pH$$

The term "*pH*" is accordingly defined as the logarithm of the reciprocal of the hydrogen-ion concentration. The *pH* value therefore can be calculated directly, in a potentiometric determination, by dividing the observed voltage by the constant 0.059.

The calculation of the *pH* value from a given value of C_{H^+} is a more or less simple matter. If, for example, a certain acidic solution, is known to have a C_{H^+} of, say, 1×10^{-4} , the conversion to *pH* is based on the following relationship.

$$\begin{aligned} pH &= \log \left(\frac{1}{1 \times 10^{-4}} \right) \\ &= \log 1 - \log (10^{-4}) \\ &= 0 - (-4) \\ &= +4 \\ &= 4 \end{aligned}$$

Note that the *pH* is merely the exponential value of the hydrogen-ion concentration with the negative sign removed. This is, indeed, a fortunate mathematical relationship, converting to the *pH* scale by simply expressing the exponent of the logarithmic relation as a positive number.

Example 3. What is the *pH* value of a solution whose hydrogen-ion concentration is $1 \times 10^{-8.75}$?

$$\begin{aligned} pH &= \log \frac{1}{1 \times 10^{-8.75}} \\ &= 0 - (-8.75) \\ &= 8.75 \end{aligned}$$

The calculation is somewhat more complicated when the value of C_{H^+} is expressed as a mixed number.

Example 4. Calculate the *pH* of a solution having a C_{H^+} of 2.6×10^{-4} .

$$\begin{aligned} pH &= \log \frac{1}{C_{H^+}} \\ &= \log \left(\frac{1}{2.6 \times 10^{-4}} \right) \\ &= \log 1 - \log 2.6 \times 10^{-4} \\ &= -(\log 2.6 \times 10^{-4}) \end{aligned}$$

It now becomes necessary to convert the coefficient 2.6 into a logarithm, in order to incorporate it as part of the exponent. The logarithm of 2.6 is + 0.41. Therefore

$$\begin{aligned} 2.6 \times 10^{-4} &= 1.0 \times 10^{-4+0.41} \\ &= 1.0 \times 10^{-3.59} \end{aligned}$$

Then
$$\begin{aligned} pH &= -(\log 1.0 \times 10^{-3.59}) \\ &= -(-3.59) \\ &= 3.59 \end{aligned}$$

In a manner analogous to the designation of C_{H+} values in terms of the pH scale, we might express hydroxyl-ion concentrations on a similar logarithmic scale. That is

$$pOH = \log \frac{1}{C_{OH-}}$$

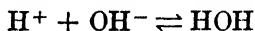
In the accompanying table (Table II), there are arranged the C_{H+} and pH values as well as the C_{OH-} and pOH values of acidic, neutral and basic solutions of varying normalities, the assumption being that the ionization of these solutions (except water) is complete.

TABLE II

Normality	C_{H+}	pH	C_{OH-}	pOH
acidic	1.0	0	10^{-14}	14
	0.1	1	10^{-13}	13
	0.01	2	10^{-12}	12
	0.001	3	10^{-11}	11
	0.0001	4	10^{-10}	10
	0.00001	5	10^{-9}	9
	0.000001	6	10^{-8}	8
	water; or neutrality			
	10^{-7}	7	10^{-7}	7
	0.000001	8	10^{-6}	6
basic	0.00001	9	10^{-5}	5
	0.0001	10	10^{-4}	4
	0.001	11	10^{-3}	3
	0.01	12	10^{-2}	2
	0.1	13	10^{-1}	1
	1.0	14	10^0	0

NEUTRALIZATION AND HYDROLYSIS

The fundamental reaction which takes place when acids and bases interact is the union of H^+ ions and OH^- ions to form water. That is



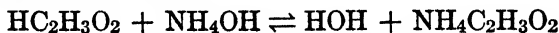
This, of course, means that, in all neutralization reactions, the water equilibrium is involved, the value of K_w must be satisfied, and equilibrium, as expressed by the relation

$$C_{H^+} \times C_{OH^-} = K_w = 1.2 \times 10^{-14}$$

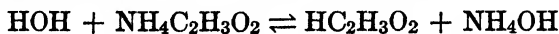
must be maintained. When equivalent quantities of an acid and base are mixed the final equilibrium is not necessarily at neutrality. Indeed, it is only for those pairs of acids and bases for which the extent of ionization is the same that final equilibrium comes at neutrality (pH of 7); all other pairs, when reacting in equivalent amounts, reach final equilibrium in the mixed solutions in either the acidic or basic region, that is, at pH values smaller or greater than 7. The final equilibrium point reached in an acid-alkali titration depends upon the nature of the salt formed in the reaction, and this, in turn, depends upon the degree of ionization of the acid and base interacting.

It is highly important to know at what pH value final equilibrium is reached, when equivalent quantities of reacting acids and bases are brought together in a titration in order that the proper indicator be selected.

In order to understand why equilibrium at the equivalent point in a titration does not always come at strict neutrality, the possibility and extent of hydrolysis of the salt resulting from the reaction must be considered. Hydrolysis may be defined as the reaction of the ions of water with the ions of salts which are formed from weakly ionized acids or bases. A hydrolysis reaction is the reverse of a neutralization reaction; in fact, in the reversible reaction between an acid and a base it is the interaction of the products of this reaction. To illustrate, when $HC_2H_3O_2$ reacts with NH_4OH



the ions of water react with the ions of $NH_4C_2H_3O_2$



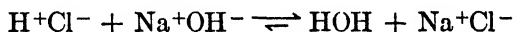
to re-form certain definite amounts of $HC_2H_3O_2$ and NH_4OH . If more non-ionized $HC_2H_3O_2$ should form than non-ionized NH_4OH , more H^+ ions are used up than OH^- ions, and the solution would then be basic. In this particular case, as shown later, the amounts of both happen to be almost the same, resulting in a solution which is practically neutral.

The calculation of the equilibrium pH value at the equivalent point in a titration is herewith illustrated for a number of different acids and bases.

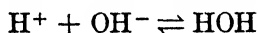
Calculation of pH at the Equivalence Point. As already noted, the pH reached in an acid-base titration depends upon the relative degree of ionization of the acid and the base, since this determines how the resulting salt will hydrolyze. Since acids and bases range widely in their extent of ionization, from practically complete to only slightly, we may expect a considerable range of pH values for different combinations of acids and bases. Four typical pairs will be discussed, namely

- A. Strong acid—Strong base.
- B. Weak acid—Strong base.
- C. Strong acid—Weak base.
- D. Weak acid—Weak base.

A. Strong Acid—Strong Base. For this combination we may take HCl and $NaOH$. Suppose we titrate 25 cc. of 0.1 N HCl with 0.1 N $NaOH$. When 25 cc. of $NaOH$ have been added, equivalent amounts will have reacted. Since both acid and base are strongly ionized (in fact we may here assume complete ionization), in the reaction

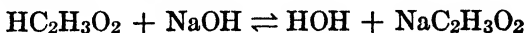


there will be little or no tendency for Na^+ ion to unite with OH^- ion to form non-ionized $NaOH$ nor will H^+ ion unite with Cl^- ion to form non-ionized HCl . Hence there will be no hydrolysis resulting. Moreover, the ionic reaction

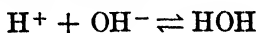


is the only one taking place and final equilibrium will be reached when the C_{H^+} and the C_{OH^-} remaining are both at a concentration of 10^{-7} . The equivalence point is at pH of 7, that is, at strict neutrality.

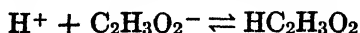
B. Weak Acid—Strong Base. As an example let us take the reaction between $HC_2H_3O_2$ and $NaOH$



The fundamental reaction, here again is



But, since when equivalent quantities are mixed there are present, in equilibrium, OH^- ions, H^+ ions and $C_2H_3O_2^-$ ions from the ionization of the salt, $NaC_2H_3O_2$, formed in the reaction. Since acetic acid is feebly ionized, there will be a definite reaction between hydrogen ions and acetate ions.



This must necessarily lower the H^+ -ion concentration in the solution, leaving an excess of hydroxyl resulting in a basic solution.

The pH of the resulting solution is calculated in the following manner: The hydrolysis is dependent upon the amount of $NaC_2H_3O_2$ formed; it is therefore simpler to arrive at the value by considering the hydrolysis of a $NaC_2H_3O_2$ solution. In an aqueous solution of $NaC_2H_3O_2$ final equilibrium depends not only on satisfying the water equilibrium

$$C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$$

but also on the acetic acid equilibrium which is controlled by its ionization constant.

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = 1.8 \times 10^{-5}$$

The hydrolysis equilibrium is then jointly controlled by the two equilibria and if we divide the former by the latter

$$\frac{C_{H^+} \times C_{OH^-}}{C_{H^+} \times C_{C_2H_3O_2^-}} = \frac{K_w}{K_{(ion)}} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$C_{HC_2H_3O_2}$$

we get the hydrolysis expression

$$\frac{C_{OH^-} \times C_{HC_2H_3O_2}}{C_{C_2H_3O_2^-}} = 6.7 \times 10^{-10}$$

where 6.7×10^{-10} is the hydrolysis constant for $NaC_2H_3O_2$, C_{OH^-} is the hydroxyl-ion concentration at equilibrium, $C_{HC_2H_3O_2}$ is the concentration of acetic acid formed in the hydrolysis and $C_{C_2H_3O_2^-}$ is the concentration of the ion of the salt formed. The value of C_{OH^-} equals that of $C_{HC_2H_3O_2}$ because for every ion of hydrogen combined to form $HC_2H_3O_2$ a hydroxyl ion is left in excess.

If in a titration we add 25 cc. of 0.1 *N* NaOH to 25 cc. of 0.1 *N* $HC_2H_3O_2$ they will have reacted in equivalent proportions. The amount of $NaC_2H_3O_2$ would be 0.1 normal, but since the volume of the mixture is now 50 cc., the concentration of the $NaC_2H_3O_2$ and hence that of the $C_2H_3O_2$ ion is 0.05 normal (or molar). Letting x stand for the OH^- concentration, as well as the acetic-acid concentration formed by hydrolysis, we have

$$\frac{x \times x}{(0.05 - x)} = 6.7 \times 10^{-10}$$

As an approximation, since the amount of $C_2H_3O_2^-$ ion combined is negligibly small, we can write

$$\frac{x^2}{0.05} = 6.7 \times 10^{-10}$$

whence

$$x = 5.8 \times 10^{-6}$$

Since

$$C_{H^+} \times C_{OH^-} = K_w$$

$$\begin{aligned} C_{H^+} &= \frac{K_w}{C_{OH^-}} \\ &= \frac{1.2 \times 10^{-14}}{5.8 \times 10^{-6}} \\ &= 2.07 \times 10^{-9} \end{aligned}$$

Moreover,

$$pH = \log \frac{1}{C_{H^+}}$$

corresponding to a pH of 8.68, or approximately 8.7.

The steps in this calculation can be shortened, for since

$$\frac{C_{OH^-} \times C_{HC_2H_3O_2}}{C_{C_2H_3O_2^-}} = \frac{K_w}{K_{(ion)}}$$

and $C_{HC_2H_3O_2}$ is equal to C_{OH^-}

$$(C_{OH^-})^2 = \frac{K_w \times C_{C_2H_3O_2^-}}{K_{(ion)}}$$

From the water equilibrium,

$$C_{OH^-} = \frac{K_w}{C_H}$$

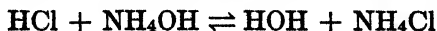
and solving for C_{H^+} ,

$$\begin{aligned} C_{H^+} &= \sqrt{\frac{K_w \times K_{(ion)}}{C_{C_2H_3O_2^-}}} \\ C_{H^+} &= \sqrt{\frac{1.2 \times 10^{-14} \times 1.8 \times 10^{-5}}{0.05}} = 2.07 \times 10^{-9} \end{aligned}$$

corresponding, as before, to a pH of 8.68.

Equivalence, in this reaction, therefore, is reached at a pH of 8.68, that is, in a basic solution.

C. Strong Acid—Weak Base. Selecting, as an example, the neutralization of HCl by NH_4OH , according to the equation



it is seen that the secondary reaction which takes place is the hydrolysis of the NH_4Cl , due to re-formation of the slightly ionized base NH_4OH . We can therefore predict that in such a neutralization reaction, final equilibrium will be reached in an acidic solution, since hydroxyl ions are removed in excess of those of hydrogen.

The $p\text{H}$ value attained at equivalence is calculated, from the hydrolysis formula, in an analogous manner as that for $\text{NaC}_2\text{H}_3\text{O}_2$. Here the water equilibrium and the ionization constant of NH_4OH are the controlling factors.

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4^+} \times C_{\text{OH}^-}} = \frac{K_w}{K_{(\text{ion})}}$$

$$C_{\text{NH}_4\text{OH}}$$

Whence

$$\frac{C_{\text{H}^+} \times C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+}} = \frac{1.2 \times 10^{-14}}{1.75 \times 10^{-5}} = 6.9 \times 10^{-10}$$

As before, if 25 cc. of 0.1 N HCl react with 25 cc. of 0.1 N NH_4OH , at equivalence, we have a 0.05 N solution of NH_4Cl .

Letting x equal the C_{H^+} as well as $C_{\text{NH}_4\text{OH}}$;

$$\frac{x \times x}{0.05} = 6.9 \times 10^{-10}$$

$$C_{\text{H}^+} = 5.9 \times 10^{-6}$$

Instead of using the value of the hydrolysis constant, equations can be combined to read

$$C_{\text{H}^+} = \sqrt{\frac{K_w \times C_{\text{NH}_4}}{K_{(\text{ion})}}}$$

and we have

$$C_{\text{H}^+} = \sqrt{\frac{1.2 \times 10^{-14} \times 5 \times 10^{-2}}{1.75 \times 10^{-5}}}$$

$$= 5.9 \times 10^{-6}$$

This corresponds to a $p\text{H}$ of 5.24.

D. Weak Acid—Weak Base. If a weak acid is allowed to react with a weak base, the $p\text{H}$ reached at equilibrium, when equivalent quantities have reacted, depends upon the relative degrees of ionization of both acid and base. If both reactants are ionized to the same extent, equal quantities of non-ionized acid and base remain at equivalence and the $p\text{H}$ value is substantially 7. This is the same as saying that the salt produced in such a reaction hydrolyzes equally in an acidic and basic direction and, when equilibrium is reached, the solution will be neutral.

This is the condition reached, practically, when $\text{HC}_2\text{H}_3\text{O}_2$ reacts in equivalent quantities with NH_4OH , since the degrees of ionization of both are approximately the same.

When there is an appreciable, but not too great a difference in the degrees of ionization of base and acid, both being slightly ionized, the C_{H^+} and from this the $p\text{H}$ value at equivalence can be calculated. The formula is here derived, in terms of the hydrolysis of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

The ionization equilibrium for the weak acid is

$$\frac{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K_{(\text{acid})}$$

and for the base

$$\frac{C_{\text{OH}^-} \times C_{\text{NH}_4^+}}{C_{\text{NH}_4\text{OH}}} = K_{(\text{base})}$$

and for water

$$C_{\text{H}^+} \times C_{\text{OH}^-} = K_w$$

Therefore

$$\frac{C_{\text{H}^+} \times C_{\text{OH}^-}}{C_{\text{H}^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-} \times \frac{C_{\text{OH}^-} \times C_{\text{NH}_4^+}}{C_{\text{NH}_4\text{OH}}}} = \frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}}$$

The expression just given is the hydrolysis equilibrium for $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. In its simpler form it is

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times C_{\text{NH}_4\text{OH}}}{C_{\text{C}_2\text{H}_3\text{O}_2^-} \times C_{\text{NH}_4^+}} = \frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}} = K_{(\text{hyd})} \quad (1)$$

Since the salt is a strong electrolyte

$$C_{\text{NH}_4^+} = C_{\text{C}_2\text{H}_3\text{O}_2^-}$$

and assuming practically equal concentrations of acid and base formed in hydrolysis

$$C_{\text{NH}_4\text{OH}} = C_{\text{HC}_2\text{H}_3\text{O}_2}$$

From equation (1) therefore

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{C_{\text{NH}_4\text{OH}}}{C_{\text{NH}_4^+}}$$

and therefore

$$\frac{(C_{\text{HC}_2\text{H}_3\text{O}_2})^2}{(C_{\text{C}_2\text{H}_3\text{O}_2^-})^2} = \frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}}$$

or

$$C_{\text{HC}_2\text{H}_3\text{O}_2} = C_{\text{C}_2\text{H}_3\text{O}_2^-} \sqrt{\frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}}}$$

The hydrolysis equation for the salt of a weak acid as given on page 66 is

$$\frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times C_{\text{OH}^-}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} = \frac{K_w}{K_{(\text{acid})}}$$

from which

$$C_{\text{HC}_2\text{H}_3\text{O}_2} = \frac{K_w \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{K_{(\text{acid})} \times C_{\text{OH}^-}} \quad (2)$$

Equating (1) and (2) since both equal $C_{\text{HC}_2\text{H}_3\text{O}_2}$

$$\begin{aligned} \frac{K_w \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{K_{(\text{acid})} \times C_{\text{OH}^-}} &= C_{\text{C}_2\text{H}_3\text{O}_2^-} \sqrt{\frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}}} \\ \frac{(K_w)^2}{(K_{(\text{acid})})^2 \times (C_{\text{OH}^-})^2} &= \frac{K_w}{K_{(\text{acid})} \times K_{(\text{base})}} \end{aligned}$$

Solving for C_{OH^-}

$$C_{\text{OH}^-} = \sqrt{\frac{K_w \times K_{(\text{base})}}{K_{(\text{acid})}}}$$

acid since $C_{\text{OH}^-} = \frac{K_w}{C_{\text{H}^+}}$

therefore

$$C_{\text{H}^+} = \sqrt{\frac{K_w \times K_{(\text{acid})}}{K_{(\text{base})}}}$$

From this equation the hydrogen-ion concentration and the pH value at equivalence can be calculated, provided that the ionization constants for the acid and base do not differ too much. In the case of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, the acid and base constants are substantially 1.8×10^{-5} , from which it follows that the pH at equivalence is practically 7.

CALCULATION OF TITRATION CURVES

There are, as pointed out on page 50, two methods by which a titration can be conducted with respect to the location of the end point. Both methods can be applied to precipitation, acidimetric, alkalimetric, as well as oxidation and reduction reactions. The older and common method is by the use of indicators which give a sharp color change when the equilibrium point of the reaction is reached, and the selection of the correct indicator depends upon knowing this equilibrium point. In acid-alkali titrations, when indicators are used, the nature of the acid or alkali being titrated furnishes the guide for the selection of the indicator. A potentiometric titration consists in measuring the changes in the

electromotive force of an electrolytic cell made up of the combination of a standard reference electrode and another electrode which is put into the solution being neutralized. As the reaction gradually runs to completion by the addition of measured quantities of the standard reagent, there will be corresponding changes in the voltage of the cell. In the case of an acid-alkali titration, a potentiometric titration consists, in fact, of a series of hydrogen-ion concentration measurements, as described on page 61, so that, when titrating an acid by a standard solution of alkali, the hydrogen-ion concentration gradually and then rapidly decreases. The change in the voltage of the cell is so rapid in the vicinity of the equilibrium point that an experienced analyst judges the end point by the abnormally large deflection of the voltmeter needle of the potentiometer. By actually recording the voltages, as the neutralization progresses and from the Nernst equation for the hydrogen electrode:

$$\text{E.M.F.} = 0.059 \log \frac{1}{C_H}$$

the hydrogen-ion concentrations, or better still, the *pH* values directly can be calculated from the relation:

$$\frac{\text{E.M.F.}}{0.059} = \log \frac{1}{C_H} = pH$$

A series of *pH* values is thus obtained. When these values are plotted on coordinate paper against added volumes of standard reagent, a graph is obtained, similar to the ones shown below. Such graphs are known as titration curves. The equivalence point and therefore the end point can then be more accurately located from the curve. The vertical portion of such a curve gives the range over which the hydrogen-ion concentration or *pH* is undergoing the most rapid change, and the bisection point of the vertical portion (the inflection point) locates the definite equilibrium point and is taken as the end point.

Curves which show graphically the changes taking place during the addition of successive volumes of reagent can also be plotted by calculation from proper data. Curves of this kind are of considerable value in following the course of a reaction and in predicting the equilibrium point which is required for the selection of the indicator in an actual titration. Such calculated curves, which are followed more or less closely in a potentiometric titration and give a general idea of the changes in an indicator titration, are shown for typical combinations of acids and bases.

The calculation of the *pH* values which show the change taking place during a neutralization reaction will now be taken up for a few typical cases.

Strong Acid-Strong Base Curve. Suppose we titrate 25 cc. of 0.1 *N* HCl with 0.1 *N* NaOH.

1. At the outset, before any base is added, the solution has a normality of 0.1. Since here we may assume complete ionization the C_{H^+} is 10^{-1} and the *pH* is 1.

2. When 5.0 cc. of 0.1 *N* NaOH have been added, there remain 20 cc. of 0.1 *N* HCl in a total volume of 30.0 cc. The normality of the solution is no longer 0.1 but is now 0.067 *N* as is seen from the inverse relation

$$20 \text{ cc.} : 30 \text{ cc.} = x : 0.1$$

or

$$V_1 N_1 = V_2 N_2$$

The C_H is 6.7×10^{-2} and the *pH* is 1.17.

3. When the solution is half neutralized, 12.5 cc. of 0.1 *N* HCl remain, now diluted to 37.5 cc. The normality of the HCl remaining is 0.033, the C_{H^+} is 3.3×10^{-2} and the *pH* is 1.48.

4. In this manner, the *pH* values recorded in Table III have been calculated.

TABLE III

THE NEUTRALIZATION OF A STRONG ACID BY A STRONG BASE

cc. NaOH added	cc. HCl remaining	Total volume of solution	Normality of solution	C_{H^+}	<i>pH</i>
0	25.0	25.0	0.100	1×10^{-1}	1.
5.0	20.0	30.0	0.066	6.6×10^{-2}	1.18
12.5	12.5	37.5	0.033	3.3×10^{-2}	1.48
20.	5.0	45.0	0.011	1.1×10^{-2}	1.96
22.5	2.5	47.5	0.0053	5.3×10^{-3}	2.28
24.0	1.0	49.0	0.0020	2.0×10^{-3}	2.70
24.5	0.5	49.5	0.0010	1.0×10^{-3}	3.00
24.9	0.1	49.9	0.0002	2.0×10^{-4}	3.70
24.95	0.05	49.95	0.0001	1.0×10^{-4}	4.00
25.0	0.0	50.0	0.0	1.0×10^{-7}	7.00
25.05	-0.05	50.05	0.0001 (NaOH)	1.2×10^{-10}	9.92
25.1	-0.1	50.1	0.0002 "	6.0×10^{-11}	10.22
26.0	-1.0	51.0	0.002 "	6.0×10^{-12}	11.22

5. Note that when but a single drop, 0.05 cc. of HCl, remains the *pH* is 4.00.

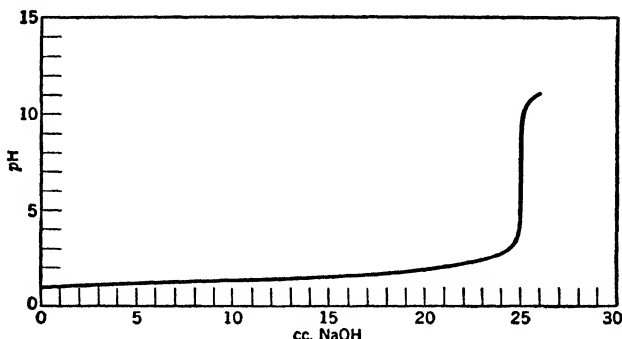
6. At equivalence, since NaCl does not hydrolyze, the *pH* will be 7.

7. A drop (0.05 cc.) of 0.1 *N* NaOH in excess, in the total volume of 50.05, now renders the solution basic, with an NaOH normality of

$$0.05 \times 0.1 = 50.05 \times x$$

$$x = 0.0001 = 1 \times 10^{-4}$$

A normality of 10^{-4} with respect to a NaOH solution means an OH-ion concentration of 10^{-4} or a C_{H^+} of 10^{-10} . The *pH* is 10.



Weak Acid-Strong Base Curve. The calculation of *pH* values, when for example 25 cc. of 0.1 *N* $\text{HC}_2\text{H}_3\text{O}_2$ are titrated with 0.1 *N* NaOH, is somewhat complicated by the fact that acetic acid is a weakly ionized acid, the presence of $\text{NaC}_2\text{H}_3\text{O}_2$ formed in the reaction acts by common-ion effect and, as previously shown, the equivalent point is displaced from neutrality because of hydrolysis.

1. The initial point can be directly calculated from the normality of the solution and its degree of ionization.

$$C_{H^+} = 0.1 \times 0.0134 = 1.34 \times 10^{-3}$$

from which *pH* = 2.9

Or, if the degree of ionization is not readily known, C_{H^+} can be obtained from the equilibrium equation:

$$\frac{C_{H^+} \times C_{\text{C}_2\text{H}_3\text{O}_2^-}}{C_{\text{HC}_2\text{H}_3\text{O}_2}} = K_{(\text{ion})}$$

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

(neglecting the small amount of $\text{HC}_2\text{H}_3\text{O}_2$ which ionizes).

Whence

$$x = 1.3 \times 10^{-3} \quad \text{and} \quad \text{pH} = 2.9$$

2. When 5 cc. of 0.1 *N* NaOH are added the total volume is 30 cc., of which 20 cc. are un-neutralized 0.1 *N* acetic acid. The new normality of the $\text{HC}_2\text{H}_3\text{O}_2$ is therefore 0.067. The $\text{C}_2\text{H}_3\text{O}_2^-$ ion concentration corresponds to 5 cc. of 0.1 *N* $\text{NaC}_2\text{H}_3\text{O}_2$ in 30 cc. or, from the inverse relation $V_1N_1 = V_2N_2$, a normality of 0.0167. Substituting these values in the equation

$$\begin{aligned} C_{\text{H}^+} &= \frac{C_{\text{HC}_2\text{H}_3\text{O}_2} \times K_{(\text{ion})}}{C_{\text{C}_2\text{H}_3\text{O}_2^-}} \\ &= \frac{0.067}{0.0167} \times 1.8 \times 10^{-5} \\ &= 7.22 \times 10^{-5} \end{aligned}$$

It will be noted that the ratio $\frac{0.067}{0.0167}$, which represents the concentra-

tion of acetic acid and acetate ion, respectively, is the same as the ratio of the volumes of 0.1 *N* solutions, namely 20 cc. of acid and 5 cc. of $\text{NaC}_2\text{H}_3\text{O}_2$. That is

$$\frac{0.067}{0.0167} = \frac{20 \text{ cc.}}{5 \text{ cc.}}$$

This simplifies the calculation, so that here, as well as at all desired points, we can substitute volumes for normalities.

3. For all points up to and including the addition of 24.95 cc. of, 0.1 *N* NaOH, the following formula can be used

$$C_{\text{H}^+} = \frac{\text{Vol. acid remaining}}{\text{Vol. NaOH added}} \times 1.8 \times 10^{-5}$$

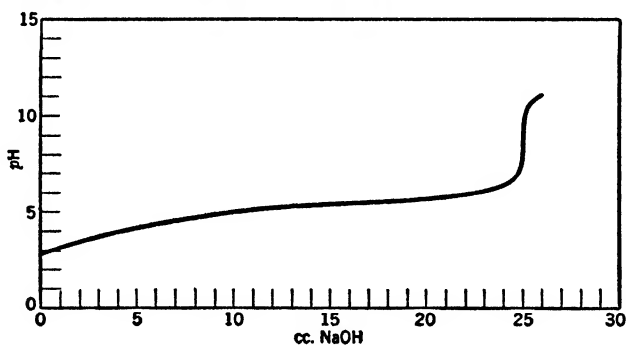
4. At the equivalent point, when 25 cc. of the base have been added, the hydrolysis determines the *pH* value. This has already been calculated, on page 67, to be 8.68.

5. Beyond the equivalent point, when an excess of base is present, the *pH* values are the same as already calculated on page 73 for the strong acid-strong base combination.

Strong Acid-Weak Base Curve. The titration of a strong acid by a standard weak base is never carried out in practice, but the reverse, the titration of weak bases such as NH_4OH by standard HCl , is of frequent occurrence. The course of the reaction is analogous to that just considered for acetic acid and NaOH, but the *pH* values are reversed. Let us consider the titration of 25 cc. of 0.1 *N* NH_4OH with 0.1 *N* HCl .

TABLE IV
NEUTRALIZATION OF A WEAK ACID BY A STRONG BASE

cc. NaOH added	cc. HC ₂ H ₃ O ₂ remaining	Total volume of solution	C_{H^+}	pH
0	25.0	25.0	1.3×10^{-3}	2.9
5.0	20.0	30.0	7.2×10^{-5}	4.1
12.5	12.5	37.5	1.8×10^{-5}	4.7
20.0	5.0	45.0	4.5×10^{-6}	5.4
22.5	2.5	47.5	2.0×10^{-6}	5.7
24.0	1.0	49.0	7.5×10^{-7}	6.12
24.5	0.5	49.5	3.7×10^{-7}	6.43
24.9	0.1	49.9	7.4×10^{-8}	7.13
24.95	0.05	49.95	3.6×10^{-8}	7.44
25.0	0.0	50.0	2.1×10^{-9}	8.7
25.05	-0.05	50.05	1.2×10^{-10}	9.9
25.1	-0.1	50.1	6.0×10^{-11}	10.2
26.0	-1.0	51.0	6.0×10^{-12}	11.2



1. The pH of the original solution may be found either from the degree of ionization or from the ionization constant. In the former case, the solution is 0.1 N and the degree of ionization (Table X) is 1.31 per cent.

$$C_{OH^-} = 0.1 \times 0.0131 = 0.00131$$

$$= 1.31 \times 10^{-3}$$

Therefore

$$C_{H^+} = \frac{1.2 \times 10^{-14}}{1.31 \times 10^{-3}} = 1 \times 10^{-11.04}$$

Therefore

$$pH^+ = 11.04$$

In the latter case, using the equilibrium

$$\frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}} = K_{(\text{don})}$$

$$C_{\text{OH}^-} = \sqrt{K_{(\text{don})} \times C_{\text{NH}_4\text{OH}}} = 1.32 \times 10^{-3}$$

Therefore,

$$C_{\text{H}^+} = \frac{K_w}{C_{\text{OH}^-}} \quad \text{and} \quad \text{pH} = \log \frac{1}{C_{\text{H}^+}}$$

$$\text{pH}^+ = 11.04$$

2. For values of pH , up to the addition of about 24.95 cc. of 0.1 N HCl , the normality of the remaining base and the normality of the NH_4Cl formed may be evaluated, or alternatively, as in the case of acetic acid, the ratio of volumes may be taken. By combining

$$K_w = C_{\text{H}^+} \times C_{\text{OH}^-} \quad \text{and} \quad K_{(\text{don})} = \frac{C_{\text{NH}_4^+} \times C_{\text{OH}^-}}{C_{\text{NH}_4\text{OH}}},$$

we have

$$C_{\text{H}^+} = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_4\text{OH}}} \times \frac{K_w}{K_{(\text{don})}}$$

For example, when 5 cc. of acid have been added there remain 20 cc. of un-neutralized NH_4OH and there were formed 5 cc. of NH_4Cl .

$$\begin{aligned} C_{\text{H}^+} &= \frac{5}{20} \times \frac{1.2 \times 10^{-14}}{1.75 \times 10^{-5}} \\ &= 1.7 \times 10^{-10} \end{aligned}$$

Therefore

$$\text{pH} = 9.77$$

Calculation of other points is left for the student.

3. The equivalent point, at a pH of 5.24 has already been established by the calculation on page 68.

4. Points beyond the equivalent volume, when an excess of acid is present, have the same pH values as already calculated, on page 73, for the HCl — NaOH combination.

Weak Acid-Weak Base Curve. Finally, the reaction between a weak acid and a weak base remains to be considered. The course of the reaction presents some interesting characteristics but, in practice, such a titration is not made, because no indicator can be employed for the titration, nor can the end point be found in a potentiometric titration.

If we take, for example, the reaction between 0.1 *N* HC₂H₃O₂ and 0.1 *N* NH₄OH the following characteristics are to be observed.

1. If the acid is being neutralized by the addition of base, the initial *pH* of the solution, as already computed on page 73 will be 2.9, and, conversely, if base is being neutralized by acid, the initial *pH* of a 0.1 *N* NH₄OH solution is 11.04.

2. *pH* values for points up to practically the equivalent point are identical with those already calculated or discussed for either the acetic acid or the ammonium hydroxide titrations as the case may be.

3. The equivalent point, since both acid and base are about equally ionized, will have a *pH* of practically 7, as already pointed out on page 70. In cases where both reactants are weakly ionized, but one is somewhat stronger than the other, the *C_H* can be calculated from the formula given on page 70.

PROBLEM SET 6

EQUILIBRIUM IN NEUTRALIZATION

101. Calculate the H⁺-ion concentration in solutions of the following mono-basic acids, the molarity, or normality and degree of ionization being given:

(a) HCl	0.1 <i>M</i>	or	0.1 <i>N</i>	94.8%	<i>Ans.</i>	9.48×10^{-2} .
(b) HNO ₂	0.1 <i>M</i>	or	0.1 <i>N</i>	8.0%		8.0×10^{-3} .
(c) HCHO	0.1 <i>M</i>	or	0.1 <i>N</i>	4.5%		4.5×10^{-3} .
(d) HC ₂ H ₃ O ₂	0.1 <i>M</i>	or	0.1 <i>N</i>	1.34%		1.34×10^{-3} .
(e) HCN	0.1 <i>M</i>	or	0.1 <i>N</i>	0.01%		1.0×10^{-5} .

102. Calculate the H-ion concentration of a 0.01 *N* solution of acetic acid which is 4.17 per cent ionized. What is the H-ion concentration of 0.01 *N* solution of HCl which is 99.8 per cent ionized?

103. Calculate the OH⁻-ion and H⁺-ion concentrations of the following solutions of bases, the normality and degree of ionization being given. $K_w = 1 \times 10^{-14}$.

				OH ⁻	H ⁺
(a) NaOH	0.1 N	90.5%	<i>Ans.</i>	9.05×10^{-2} .	1.11×10^{-13} .
(b) KOH	0.01 N	93.5%		9.35×10^{-3} .	1.07×10^{-12} .
(c) NH ₄ OH	0.001 N	11.7%		1.17×10^{-4} .	8.55×10^{-11} .

104. Calculate the OH⁻-ion and H⁺-ion concentrations in solutions of NH₄OH of the following normalities and degrees of ionization. $K_w = 1 \times 10^{-14}$.

(a) 1.0 <i>N</i>	0.4 %
(b) 0.1 <i>N</i>	1.31%
(c) 0.01 <i>N</i>	4.07%
(d) 0.001 <i>N</i>	11.7 %

105. For the following solutions, the H⁺-ion concentrations of which are given express the acidity in terms of *pH* value.

Solution	C_{H^+}	Ans. pH
(a) HCl	9.48×10^{-2}	1.02.
(b) HNO_2	8.0×10^{-3}	2.1.
(c) HCHO	4.5×10^{-8}	2.35.
(d) $HC_2H_3O_2$	1.34×10^{-8}	2.87.
(e) HCN	1×10^{-5}	5.00.

106. Find the pH values for the following bases having the H-ion concentration corresponding to the normalities given.

(a) NaOH	1.11×10^{-13}	0.1 N
(b) KOH	1.07×10^{-12}	0.01 N
(c) NH_4OH	8.55×10^{-11}	0.001 N

107. Suppose that you mixed 20.00 cc. of 0.1 N NaOH with 30.00 cc. of 0.1 N HCl. What would be (a) the H-ion concentration, and (b) the pH value of the resulting mixture, assuming complete ionization?

Ans. (a) 2×10^{-2} . (b) 1.70.

108. If to 25.00 cc. of 0.1 N NaOH you added 12.50 cc. of 0.1 N HCl, what would be (a) the OH-ion concentration, (b) the H-ion concentration and (c) the pH value of the resulting mixture, assuming complete ionization?

109. Calculate (a) the H-ion concentration and (b) the pH value of a 0.01 N solution of $NaC_2H_3O_2$. $(C_{H^+} \times C_{C_2H_3O_2^-})/C_{HC_2H_3O_2} = 1.8 \times 10^{-5}$; $C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$.

Ans. (a) 4.76×10^{-9} . (b) 8.34.

110. Calculate the pH value of a 0.01 N solution of NH_4Cl .

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = 1.75 \times 10^{-5}. \quad C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}$$

111. Calculate the pH value of the mixture when 25.00 cc. of 0.1 N HCl are mixed with 75.00 cc. of 0.1 N NH_4OH .

$$(C_{NH_4^+} \times C_{OH^-})/C_{NH_4OH} = 1.75 \times 10^{-5}. \quad C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}.$$

Ans. 9.48.

112. What is the pH value of the mixture obtained by adding 50.00 cc. of 0.5 *M* NaOH to 50.00 cc. of 0.5 N $HC_2H_3O_2$?

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = 1.8 \times 10^{-5}. \quad C_{H^+} \times C_{OH^-} = 1.2 \times 10^{-14}.$$

113. Suppose you were titrating 25.00 cc. of 0.1 N $HC_2H_3O_2$ with 0.1 N NaOH. (a) What would be the pH value of the acid before titration was begun (degree of ionization 1.3 per cent)? (b) What would be the pH of the solution when one half of the equivalent of NaOH (12.50 cc.) had been added? (c) When 0.9 of the acid had been neutralized?

Ans. 2.89; 4.74; 5.70.

114. If you were titrating 50.00 cc. of 0.1 N HCl with 0.1 N NaOH, what would be the pH value (a) when 30.00 cc. of the NaOH solution were added, (b) when 47.50 cc. NaOH were added and (c) when 49.90 cc. NaOH were added. Assume complete ionization.

115. If, for convenience, we mix solutions of 0.1 *N* NH_4OH and 0.1 *N* HCl in such proportions that the total volume of solution is 100 cc. What will be the *pH* (a) when we mix 55.0 cc. acid and 45.0 cc. base; (b) when 50.00 cc. of each are mixed; and (c) when 40.0 cc. of acid are mixed with 60.00. of base? $K_w = 1.2 \times 10^{-14}$; $K_{(\text{ion})} \text{NH}_4\text{OH} = 1.75 \times 10^{-5}$. *Ans.* (a) 2.0. (b) 5.24. (c) 8.88.

116. If we mix solutions of 0.1 *N* NaOH and 0.1 *N* $\text{HC}_2\text{H}_3\text{O}_2$ in the following proportions, what will be the *pH* values of the resulting mixtures? (a) 65.0 cc. acid and 35.0 cc. base; (b) 50.0 cc. of each; and (c) 10.0 cc. of acid and 90.0 cc. of base. $K_w = 1.2 \times 10^{-14}$. $K_{(\text{ion})} \text{HC}_2\text{H}_3\text{O}_2 = 1.8 \times 10^{-5}$.

117. Calculate the *pH* of the mixture when 12.50 cc. of 0.1 *N* HCl have been added to 25.00 cc. of 0.1 *N* NH_4OH . *Ans.* 9.2.

118. Imagine you are titrating 25.00 cc. of a 0.1 *N* NH_4OH solution with 0.1 *N* HCl . What are the *pH* values when (a) 5 per cent, (b) 60 per cent, (c) 90 per cent and (d) 99.9 per cent of the base have been neutralized.

119. If you mix equivalent volumes of a base, whose $K_{(\text{ion})}$ is 1×10^{-5} , with an acid, whose $K_{(\text{ion})}$ is 1×10^{-7} , what will be the *H-ion* concentration of the mixture? *Ans.* 1.09×10^{-6} .

120. Calculate the hydrolysis constant for $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

C. ADJUSTMENT OF SOLUTIONS; MIXED ALKALI CALCULATIONS

Solutions prepared and standardized for titration purposes are rarely of the exact strength desired. That is, they usually are of the approximate strength called for, but, of course, their exact strength becomes known upon standardization and they are then used without further adjustment of concentration. It sometimes becomes necessary or desirable to adjust the concentration to some definite desired value by addition of water or solute.

For example, suppose that it is desired to change the strength of an HCl solution which is 0.1019 *N* to one which is exactly 0.1 *N*. How much water must be added to 700 cc. of the 0.1019 *N* hydrochloric-acid solution in order to have a solution of the desired normality?

The diluted solution must contain 0.0036465 gram of HCl per cubic centimeter in order to be 0.1 *N*. The undiluted solution contains $0.036465 \times 0.1019 = 0.003716$ gram per cubic centimeter, and in 700 cc. there are $0.003716 \times 700 = 2.60$ grams of HCl . This quantity of pure HCl must be present in a volume of diluted solution such that each cubic centimeter contains 0.0036465 gram of HCl . If *x* represents the volume of diluted solution, then

$$0.0036465 \times x = 2.60$$

$$x = 713.3 \text{ cc.}$$

Then

$$713.3 - 700.0 = 13.3 \text{ cc., the amount of water to be added}$$

Since the normality is inversely proportional to the volume, the volume of dilute solution can also be directly calculated from the relation:

$$700 : x = 0.1 : 0.1019$$

$$x = 713.3 \text{ cc.}$$

and the volume of water to add is 13.3 cc.

Such calculations are made on the assumption that no shrinkage in the total volume takes place on mixing.

Adjustment of Solution to Read Percentage Directly. In many routine and industrial analyses it is desirable to adjust either the weight of sample or the strength of the titrating solution so that the volume of standard solution will indicate directly the percentage of the desired constituent or bear a simple relation to the percentage. The problem resolves itself into either finding how much solute is needed in making a solution for titrating a definite weight of sample so that each cubic centimeter of solution used in titrating the sample should represent 1 per cent of the desired constituent, or else fixing the weight of sample that must be taken so that with a specified strength of the solution each cubic centimeter volume used should represent 1 per cent of the desired constituent.

As an example take the following case:

How much HCl must be contained in a cubic centimeter of solution so that, with a 1-gram sample of impure Na_2CO_3 , each cubic centimeter used in titrating the sample represents 1 per cent of Na_2CO_3 ?

From the equation:

$$\frac{1 \text{ cc.} \times \text{Na}_2\text{CO}_3\text{-titre of the HCl solution}}{1 \text{ gram}} \times 100 = 1 \text{ per cent}$$

we have

$$\frac{1 \times 0.01}{1} \times 100 = 1 \text{ per cent}$$

The value of 1 cc. of the solution in terms of Na_2CO_3 is therefore 0.01.

Then $\frac{2 \text{ HCl}}{\text{Na}_2\text{CO}_3} \times 0.01 = \text{value of 1 cc. in terms of HCl, or 0.00688 gram.}$

A liter of this solution must contain 6.88 grams of HCl.

If a 2-gram sample is used, and each cubic centimeter is to indicate 1 per cent, the strength of the solution must be twice as great.

Instead of adjusting the strength of the solution, which is a tedious matter experimentally, the weight of sample may be adjusted so that, with a solution of given strength, the volume of solution used represents directly the percentage of the desired constituent.

What weight of sample of soda ash should be taken so that, when titrated with a hydrochloric-acid solution having a HCl-titre of 0.01820, each cubic centimeter should represent 1 per cent of Na_2CO_3 ?

Since:

$$\frac{1 \text{ cc.} \times 0.01820 \times \frac{\text{Na}_2\text{CO}_3}{2\text{HCl}}}{\text{Weight of sample}} \times 100 = 1 \text{ per cent}$$

the weight of sample is found to be 2.6450 grams.

The same adjustments may be made on a normality basis.

What must be the normality of a hydrochloric-acid solution so that, when a 2-gram sample of soda ash is titrated, each cubic centimeter of HCl represents 1 per cent of Na_2CO_3 ? From the general relation:

$$\frac{\text{Volume used} \times \text{Normality} \times \text{Milliequivalent weight}}{\text{Weight of sample}} \times 100 = \text{Percentage}$$

we have:

$$\frac{1 \text{ cc.} \times N \times \frac{\text{Na}_2\text{CO}_3}{2 \times 1000}}{2.0} \times 100 = 1 \text{ per cent}$$

from which $N = 0.3773$.

What weight of soda ash must be taken in order that the volume of a 0.5 N HCl solution should represent the percentage of Na_2CO_3 ?

$$\frac{1 \text{ cc.} \times 0.5 \times 0.053}{\text{Weight of sample}} \times 100 = 1 \text{ per cent}$$

from which the weight of sample required is 2.650 grams.

Calculations of Mixed Alkalies. In the usual method of calculating the alkaline strength of a basic material, the total alkalinity is computed in terms of the percentage of the constituent which predominates. For example, in the analysis of soda ash, which is largely Na_2CO_3 , but, besides inert material, usually contains small amounts of NaHCO_3 , the result is reported as percentage of Na_2CO_3 , whereas in reality both alkaline substances react with the acid used for neutralization. In cases of mixed alkalies, such as mixtures of the alkali hydroxides, carbonates and bicarbonates, the separate amounts of each constituent may be determined by titrations involving the use of two indicators.

The following possibilities may occur with the above alkalies using the sodium compounds as typical in samples which may also contain inert impurities such as chlorides and sulfates:

1. NaOH as the only alkaline substance.

2. NaHCO_3 as the only alkaline substance.
3. Na_2CO_3 as the only alkaline substance.
4. Mixtures of NaOH and Na_2CO_3 .
5. Mixtures of NaHCO_3 and Na_2CO_3 .

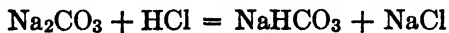
Besides these, we may have dry mixtures of NaOH and NaHCO_3 or dry mixtures of NaOH , NaHCO_3 and Na_2CO_3 , but these mixtures cannot exist in solutions because the hydroxide will react with the bicarbonate to form the carbonate. Samples covering the above five cases can be identified and the percentages of the constituents determined by the behavior of methyl orange and phenolphthalein indicators toward these alkalis during titration.

1. *Sodium Hydroxide.* This base behaves alike toward both indicators so that, when a titration is conducted with standard HCl , the end point comes at practically the same volume of added acid when methyl orange is used as when phenolphthalein is used. Complete neutralization is indicated when methyl orange turns pink and phenolphthalein turns colorless.

2. *Sodium Bicarbonate.* This base is practically neutral toward phenolphthalein. This is because the hydrogen-ion concentration derived from the weakly ionized HCO_3^- ion ($\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$) has about the concentration, 1×10^{-9} , necessary to change the color of this indicator, so that a minute amount of HCl is sufficient to indicate a neutral solution when phenolphthalein is present.

Methyl orange, however, does not change color from alkaline to acid until a concentration of hydrogen ion of about 1×10^{-4} is reached. This will occur only when the bicarbonate is actually neutralized. A titration of bicarbonate with standard acid can therefore be made only with methyl orange as indicator.

3. *Sodium Carbonate.* With phenolphthalein present, in a cold solution, a titration of sodium carbonate with standard HCl will show an end point when the solution is only one half neutralized, that is, when the Na_2CO_3 has been transformed into NaHCO_3 , thus:



The volume of acid used will therefore be one half of the total amount required for complete neutralization.

With methyl orange the end point does not come until complete neutralization takes place.

4. *A Mixture of NaOH and Na_2CO_3 .* Remembering from the foregoing cases that methyl orange changes color at complete neutralization for any alkali and that phenolphthalein shows a neutral reaction against

NaHCO_3 , the behavior of the above mixture can be easily deduced. When the mixture is titrated with acid, in the cold, in the presence of phenolphthalein as indicator, all the NaOH and one half of the Na_2CO_3 will have been neutralized when the pink color is discharged. A second titration, using methyl orange, will give the total volume of acid required for complete neutralization of both bases. The following problem will show the method of calculation.

A 0.2-gram sample of a mixture of NaOH , Na_2CO_3 and impurities was dissolved in water and then titrated cold with 0.1 N HCl , using phenolphthalein as indicator. The volume of acid required was 30.00 cc. Another 0.2-gram sample of the mixture was taken, dissolved in water and titrated with 0.1 N HCl , using methyl orange as indicator. This second titration required 40.00 cc. of the acid. What were the percentages of NaOH and Na_2CO_3 in the sample?

Since the total volume of acid required for complete neutralization of both compounds was 40.00 cc., and the volume required for the complete neutralization of NaOH plus the neutralization of one half of the Na_2CO_3 was 30.00 cc., the difference in volume between the first and the second titration was 10 cc., which represents the volume required for one half of the Na_2CO_3 . Therefore the volume required for the complete neutralization of the Na_2CO_3 is 20 cc., and the volume required for the complete neutralization of the NaOH is likewise 20 cc. The milliequivalent weight of NaOH is 0.04000, and the milliequivalent weight of Na_2CO_3 is 0.0530.

Therefore

$$\frac{20.00 \text{ cc.} \times 0.1 \times 0.04000}{0.2 \text{ gram}} \times 100 = 40.00 \text{ per cent of NaOH}$$

and

$$\frac{20.00 \text{ cc.} \times 0.1 \times 0.0530}{0.2 \text{ gram}} \times 100 = 53.00 \text{ per cent of Na}_2\text{CO}_3$$

5. *A Mixture of Na_2CO_3 and NaHCO_3 .* If a mixture of Na_2CO_3 and NaHCO_3 is titrated with acid, using phenolphthalein indicator in a cold solution, the end point will come when one half of the Na_2CO_3 is neutralized, which is equivalent to the transformation of all the carbonate into bicarbonate. The bicarbonate originally present, as well as that formed from the carbonate, will be neutral toward this indicator. A second titration, in the presence of methyl orange, will give an end point when both compounds are completely neutralized.

As an example, suppose that a 0.2-gram sample of a mixture of Na_2CO_3 , NaHCO_3 with inert material was titrated with 0.1 N HCl ,

using phenolphthalein as indicator. The volume of acid required was 10.00 cc. When the sample was titrated with methyl-orange indicator the volume of 0.1 *N* HCl required for complete neutralization was 30.00 cc.

Since in the first titration the Na_2CO_3 was half neutralized and none of the bicarbonate reacted with the acid, the volume of acid required for complete neutralization of the Na_2CO_3 is 2×10.00 , or 20.00 cc. In the second titration, since a total of 30.00 cc. of acid was required and 20.00 cc. of this were used by the Na_2CO_3 , the volume required for the NaHCO_3 was 10.00 cc. The milliequivalent weight of Na_2CO_3 is 0.0530, and that of NaHCO_3 is 0.0840.

Therefore

$$\frac{20.00 \text{ cc.} \times 0.1 \times 0.0530}{0.2 \text{ gram}} \times 100 = 53.00 \text{ per cent of } \text{Na}_2\text{CO}_3$$

and

$$\frac{10.00 \text{ cc.} \times 0.1 \times 0.0840}{0.2 \text{ gram}} \times 100 = 42.00 \text{ per cent of } \text{NaHCO}_3$$

Volume Relationships. The relationships in the volumes of acid used may be summarized as follows:

Volume Relation	Substance
Same volume for both indicators.....	NaOH
No volume for P.P.....	NaHCO_3
Twice the volume for M.O. as for P.P.....	Na_2CO_3
More than half the total volume for P.P.....	NaOH and Na_2CO_3
Less than half the total volume for P.P.....	NaHCO_3 and Na_2CO_3

The important fact, which is the key to the solution of mixed-alkali and double-indicator problems, is that phenolphthalein is neutral to bicarbonates when used in a cold solution.

PROBLEM SET 7

ADJUSTMENT OF SOLUTIONS; MIXED ALKALI CALCULATIONS

121. What volume of water would you add to 950 cc. of a 0.1267 *N* HCl solution in order to make it exactly 0.1 *N*? *Ans.* 253 cc.

122. If an HCl solution has a Na_2CO_3 -titre of 0.02578 and 750 cc. are available, what volume of concentrated HCl (sp. gr. 1.19) should be added in order to make it 0.5 *N*?

123. How much pure NaOH should be added to 800 cc. of 0.09500 *N* solution in order to make it exactly 0.1 *N*? *Ans.* 0.1600 gram.

124. A solution was prepared by dissolving 8.5 grams of NaOH and 6.2 grams of

KOH in water and diluting to 1 liter. How much of either substance should be added in order to make the solution exactly 0.5 *N*?

125. Suppose 500 cc. of 0.4678 *N* NaOH are mixed with 500 cc. of 0.5473 *N* NaOH. What is the normality of the resulting mixture, assuming one liter of mixture? How much water must be added to a liter of this mixed solution in order to make it 0.5 *N*?
Ans. 0.5076 *N*; 15 cc.

126. In a certain determination of a basic sample in which exactly 50.00 cc. of 0.1185 *N* H₂SO₄ were added (this volume known to be excess for the neutralization) a back titration with 8.50 cc. of 0.1326 *N* NaOH was employed. If the normalities had been the same, what volume of NaOH solution would have been used?

127. A hydrochloric-acid solution was found to contain 3.7550 grams of pure HCl per liter. If it is desired to dilute this solution so that the Na₂CO₃-titre is 0.005300, how much water should be added to 950 cc. of this solution?
Ans. 28.5 cc.

128. In titrating a 1-gram sample of impure Na₂CO₃ with HCl, what must be the normality of the acid in order that each cubic centimeter should represent 2 per cent of Na₂CO₃?

129. What weight of soda ash should be taken for analysis so that, when titrated with 0.1258 *N* HCl solution, the volume of acid required will equal directly the percentage of Na₂CO₃ in the sample?
Ans. 0.6668 gram.

130. If, in titrating 1-gram samples of caustic soda (NaOH) with standard H₂SO₄, what should be the NaOH-titre of the standard H₂SO₄ used in order that each cubic centimeter will represent 0.5 of 1 per cent of NaOH?

131. If a sample is known to consist of equal parts by weight of NaOH and Na₂CO₃ and 0.2-gram samples are taken for analysis, what volumes of 0.1 *N* HCl will be required for titration, using respectively, phenolphthalein in the cold and methyl orange as indicators?
Ans. 34.44 cc.; 43.87 cc.

132. A sample of material known to be either NaOH, NaCO₂ or NaHCO₃ was titrated with standard HCl. In the first titration, using phenolphthalein, in a cold solution, the volume of acid required was 20 cc. In a second titration, using the same weight of sample, but methyl orange as indicator, the volume of acid required was 40 cc. What substance was present?

133. A 1-gram mixture of equal parts of Na₂CO₃ and NaHCO₃ is titrated using phenolphthalein. Another 1-gram sample is titrated using methyl orange. What volumes of 0.5564 *N* H₂SO₄ are required in each titration?
Ans. 8.48 cc.; 27.64 cc.

134. A sample of soda ash, consisting of Na₂CO₃, NaHCO₃ and inert impurities, was subjected to differential titration. If 1.224-gram samples are titrated, respectively, with phenolphthalein in the cold, and with methyl orange as indicators, using 20.52 cc. of 0.5 *N* HCl in the first titration and 43.44 cc. of the acid in the second titration, what are the percentages of the two alkaline constituents in the sample?

✓**135.** A 2-gram sample of impure NaOH was dissolved and diluted to 500 cc. 100 cc. of this solution required 47.23 cc. of an HCl solution which has a Na₂CO₃-titre of 0.0050, using phenolphthalein as indicator. Methyl orange was then added and

the titration continued until this second indicator changed color, requiring an additional 2.50 cc. of the acid. What were the percentages of NaOH and Na_2CO_3 present?

Ans. 6.25 per cent Na_2CO_3 ;
42.21 per cent NaOH.

136. Impure caustic potash (KOH) usually contains, in addition to inert impurities, some K_2CO_3 . Suppose a 5-gram sample were dissolved, diluted to 250 cc. and aliquot volumes of 50 cc. each taken for titration. The acid used had a KOH-titre of 0.02194. If the sample contained 90.00 per cent of KOH and 2.00 per cent of K_2CO_3 , what volume of acid are required for the cold, phenolphthalein and the methyl-orange titration?

137. A sample of impure KHCO_3 weighing 1.1250 grams required 8.82 cc. of 0.1255 *N* HCl for a phenolphthalein titration. A 1.500-gram sample required 72.25 cc. of 0.1255 *N* HCl for a methyl orange titration. Calculate the percentages of KHCO_3 and K_2CO_3 .

Ans. 13.60 per cent K_2CO_3 ;
40.80 per cent KHCO_3 .

138. If 35.00 cc. of a HCl solution are required for the titration, using methyl orange as indicator, of a 1-gram sample of a mixture containing equivalent amounts of Na_2CO_3 and NaHCO_3 , what is the normality of the solution?

139. A mixture of equimolecular amounts of NaOH and Na_2CO_3 was titrated, with methyl orange as indicator. What volume of 1 *N* HCl solution was required for the neutralization of a sample weighing 1.4600 grams?

Ans. 30 cc.

140. A mixture of pure NaHCO_3 and Na_2CO_3 required 17.28 cc. of 0.4024 *N* HCl for the titration of 1.4268 grams of the mixture when phenolphthalein was used in a cold solution. An additional volume of 38.12 cc. of the acid was required, with methyl orange as indicator. What amounts of the two substances were present in the mixture?

CHAPTER VI

THE CALCULATIONS OF OXIDATION AND REDUCTION PROCESSES

There are so many substances which can be quantitatively oxidized or reduced and such a considerable number of excellent reagents available that it is not surprising that these methods are the most numerous in the entire field of quantitative analysis. The stoichiometric calculations, common to all volumetric procedures and already amply illustrated for precipitation and neutralization methods, are practically identical throughout and need not be discussed here in great detail. The same considerations in regard to the preparation and standardization of the titrating solutions and the final calculation of the results of a determination apply equally well to oxidation and reduction processes. One may employ, as a matter of personal choice, either the titre system or the normality system in standardization and in the calculation of the final result. It is to the advantage of the student to become thoroughly familiar with both.

For any analytical method, one must know the reaction upon which the method is based. The chemical equation for the reaction must be written in order that the stoichiometric relationships are clearly indicated. It is particularly important that the equation for an oxidation-reduction reaction be written especially where the normal system is to be used. The balancing of such equations frequently gives the student some difficulty.

Reactions, in aqueous solutions, take place either because ions unite or ions gain or lose electrons. An oxidation takes place when an ion loses electrons; reduction when electrons are gained. An oxidation-reduction reaction is therefore the exchange of electrons from the reducing ion to the oxidizing ion. This manifests itself in a change of valence. The valence of a reducing agent is increased in a positive direction when it is oxidized because it has lost one or more negative charges (electrons). Conversely, an oxidizing agent, by gaining one or more electrons, suffers a decrease in positive valence, i.e., an increase in a negative direction.

To write and balance the equations for oxidation-reduction reactions, the molecular formulas for the reactants and products of reaction are first

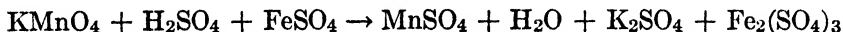
set down. Second, the unbalanced equation is rewritten in ionic form. Third, the change undergone by the oxidizing ion, showing the number of electrons gained, is written as a partial or half-cell reaction. Fourth, the reducing ion receives similar treatment. Fifth, by adding the two half-cell reactions and canceling out the number of electrons gained in the one half-cell reaction and lost in the other half-cell reaction, the completed ionic equation can usually be assembled, adjustment being made if necessary for the hydrogen or hydroxyl ions or water involved. Sixth, the balanced molecular equation is then written.

Obviously, in balancing such equations, the electron transfer must be determined. In other words, the most important matter to decide is how many electrons are lost by one component and gained by the other. There are two somewhat different, yet interdependent, ways of finding the number of electrons exchanged. One of these is to determine the valence change undergone by the atom in question; the other is a purely electrical method of balancing positive and negative charges on the ions. The former is the valence-electron method and the latter the ion-electron method.

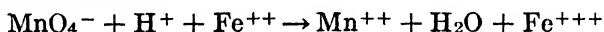
These methods are illustrated in the following example.

Example 1. Balance the equation for the reaction between KMnO_4 and ferrous sulfate in an acidified solution.

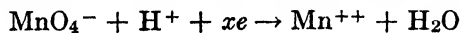
In this reaction, considered from a molecular standpoint, the ferrous sulfate is oxidized by the potassium permanganate to ferric sulfate, the permanganate is reduced to manganous sulfate, together with the formation of water and potassium sulfate. In unbalanced form the molecular equation is



The actual ionic change is

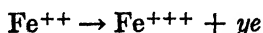


thus stripping the equation of its unessential components. The change undergone by the MnO_4^- is represented by the half-cell reaction



where xe represents the number of electrons required for the change.

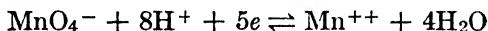
The change for the ferrous ion is



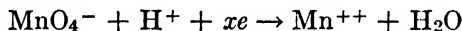
where ye represents the number of electrons given up by one ferrous ion.

From a valence-change standpoint, the valence of manganese in

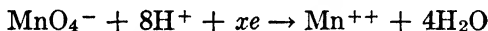
KMnO_4 is $+7$, since in the neutral molecule we have $\text{K}^{+1}\text{Mn}^{+7}\text{O}_4^{-8}$, and this on reduction in an acidified solution, goes to a valence of 2 in the Mn^{++} ion. A valence decrease of 5 takes place. Therefore 5 electrons are required for the change. The 4 oxygens require 8H^{+} to form $4\text{H}_2\text{O}$. The balanced half-cell reaction is therefore



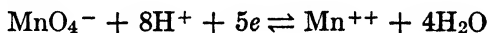
In the ion-electron method, the electrical charge on the ions as units is considered. For the same half-cell reaction



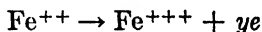
the hydrogens and oxygens are first balanced chemically, requiring 8H^{+} to react with 4O to produce $4\text{H}_2\text{O}$, the water being electrically neutral:



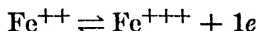
For this reaction to be electrically neutral, we have on the right 2 positive charges and on the left 1 negative charge on the MnO_4 ion and 8 positive charges on the hydrogen ions or a net charge of $+7$. This obviously required 5 negative charges (electrons) for neutrality, and the value of x , now arrived at without valence considerations of the manganese in the KMnO_4 , is as before, namely 5 . The completed half-cell reaction is therefore



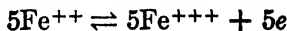
In the other half-cell reaction



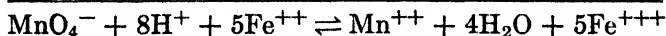
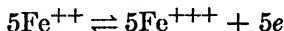
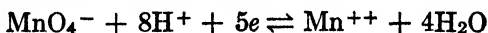
it is evident that the oxidation of one ferrous ion to the ferric state is the result of the loss of one electron. Therefore



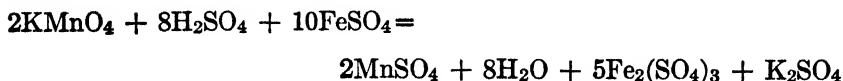
In order to supply the 5 electrons needed for the reduction of one ion of MnO_4^{-} , 5 ferrous ions are oxidized, hence



Completing the ionic equation:



The molecular equation can now be written providing for all products:



the ionic equation having been doubled for the sole purpose of providing a balance for the potassium and sulfate ions.

In simple cases, which do not involve oxy-ions and where the valence changes are self evident, the valence-electron method is the simpler. In other cases, especially where the valence is not readily ascertained by inspection, the ion-electron method is preferable.

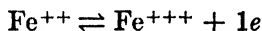
Equivalent Weights and Normal Solutions. A gram-equivalent weight is defined as that weight of substance which will involve, directly or indirectly, 1.008 grams of hydrogen. When an atom of hydrogen is oxidized to hydrogen ion, an electron is given up:



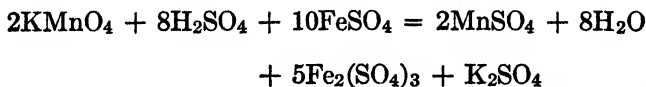
and this means that the gram-equivalent weight, 1.008 grams, of hydrogen is associated with one electron transfer. Hence for oxidizing and reducing substances, to be equivalent to this, the gram-atomic or gram-molecular weight is divided by the number of electrons lost or gained. This corresponds to the change in valence.

Example 2. What is the gram-equivalent weight of iron?

In all reactions in which iron is oxidized or reduced the ionic change is



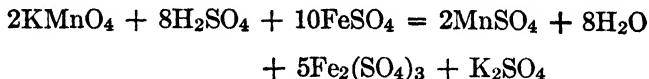
The number of electrons lost or gained is one per ion. The gram-atomic weight therefore constitutes a gram-equivalent weight and the gram-equivalent weight of any compound of iron must contain one gram-atomic weight of iron (55.84 grams). Applied specifically to the reaction



when 10FeSO_4 are involved, the gram-equivalent would be $\frac{10\text{FeSO}_4}{10}$, or one gram-molecular weight of FeSO_4 .

Example 3. What weight of KMnO_4 , to be used in an acidified solution, should be taken for the preparation of a liter of normal solution? In other words, calculate the gram-equivalent weight of KMnO_4 when

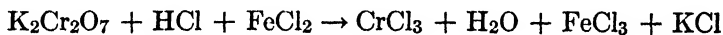
used in a reaction, such as in the determination of iron, as shown in the equation



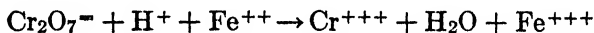
Since the number of electrons gained by one ion of MnO_4^- , or one molecule of KMnO_4 , is 5, as shown in the half-cell reaction on page 89, the equivalent weight is one-fifth of the gram-molecular weight (or, as in the reaction above, $\frac{2\text{KMnO}_4}{10}$). This is $\frac{158.03}{5}$, or 31.61 grams.

Example 4. What weight of $\text{K}_2\text{Cr}_2\text{O}_7$ would be required to make a liter of 0.1 *N* solution of this reagent to be used in the oxidation of ferrous ion?

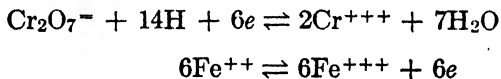
The reaction, in unbalanced form, is



Rewritten in ionic form it is:



The electron exchange is determined from the half-cell reactions



and the balanced molecular equation becomes



From this it is seen that 6 electrons are required to reduce the $\text{Cr}_2\text{O}_7^{--}$ ion to the Cr^{+++} state, or each chromium atom is decreased in valence from +6 to +3. The molecular weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is therefore divided by 6. The gram-equivalent weight is therefore $\frac{294.21}{6}$, or 49.03 grams, and for a liter of exactly 0.1 *N* solution there would be needed 4.903 grams.

Oxidation-Reduction Reactions Applied to Volumetric Methods of Determination. Among the oxidizing agents which are extensively employed in the form of standard solutions are potassium permanganate, potassium dichromate, iodine, potassium iodate and potassium bromate. Reducing agents, employed in conjunction with these oxidizing solutions and usually added as standardized solutions, are ferrous sulfate, oxalic acid, sodium thiosulfate and sodium arsenite; potassium iodide is

extensively used in unstandardized form for the liberation of iodine in iodometric methods (see page 94).

The uses of these reagents, and the calculations involved in their use, are taken up in some detail in the following sections.

Dichromate and permanganate methods will be considered first. Methods involving the halogens will then be taken up. The chapter on oxidation and reduction methods closes with additional applications.

DICHROMATE AND PERMANGANATE METHODS

Many important methods of determination are based on the oxidation of the constituent by standard solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 and reduction by FeSO_4 and $\text{H}_2\text{C}_2\text{O}_4$. These standard reagents are usually employed in conjunction with each other in the following pairs:

Dichromate with ferrous sulfate.

Permanganate with ferrous sulfate.

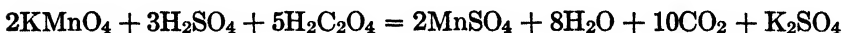
Permanganate with oxalic acid.

The derivation of the gram-equivalent weights for KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and FeSO_4 has already been discussed, along with the preparation of solutions of these reagents.

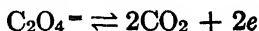
Standardization of dichromate solutions may be made with electrolytic iron, although pure $\text{K}_2\text{Cr}_2\text{O}_7$ is now procurable for direct preparation of solutions of desired strength. Permanganate solutions may be standardized with electrolytic iron, but pure $\text{Na}_2\text{C}_2\text{O}_4$ is more desirable. The reducing solutions are usually standardized by secondary standardization against the oxidizing reagents.

Example 5. How much $\text{Na}_2\text{C}_2\text{O}_4$ should be used for the standardization of an approximately 0.2 *N* solution of KMnO_4 if not more than 40 cc. of the permanganate solution are to be used?

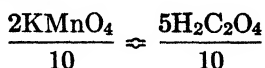
In the process, the sodium oxalate is acidified with H_2SO_4 , thus producing free $\text{H}_2\text{C}_2\text{O}_4$. The reduction of the permanganate then proceeds according to the reaction



The electron loss of the oxalate ion is



and the equivalent ratios are



giving the equivalent weight of $\text{H}_2\text{C}_2\text{O}_4$ as $\frac{\text{H}_2\text{C}_2\text{O}_4}{2}$ and, for $\text{Na}_2\text{C}_2\text{O}_4$, one half of its gram-molecular weight. The equivalent weight of $\text{Na}_2\text{C}_2\text{O}_4$ is approximately 67 grams and the milliequivalent weight 0.067 gram. For the anticipated volume of 40 cc. of a 0.2 *N* solution, the weight of $\text{Na}_2\text{C}_2\text{O}_4$ required is therefore

$$0.067 \times 0.2 \times 40 = 0.5360 \text{ gram}$$

PROBLEM SET 8

CALCULATIONS OF DICHROMATE AND PERMANGANATE PROCESSES

141. Calculate (a) the Fe-titre; (b) the Fe_2O_3 -titre; (c) the FeSO_4 -titre of a 0.2500 *N* solution of KMnO_4 .

Ans. (a) 0.01396; (b) 0.01996; (c) 0.03796.

142. If 27.25 cc. of a FeSO_4 solution are equivalent to 28.50 cc. of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the latter is exactly 0.1 *N*, what is the normality of the FeSO_4 solution?

143. If 0.2240 gram of pure iron is used in the standardization of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution and 35.00 cc. of the solution are employed, what is (a) the Fe-titre and (b) the normality of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution?

Ans. (a) 0.006400; (b) 0.1146 *N*.

144. What weight of iron wire 99.87 per cent pure should be used for the standardization of an approximately 0.1 *N* solution of $\text{K}_2\text{Cr}_2\text{O}_7$ if not more than 37.00 cc. are to be employed in the titration?

145. How many grams of $\text{K}_2\text{Cr}_2\text{O}_7$ and of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ will be required for the preparation of liter quantities of 0.1500 *N* solutions?

Ans. 7.356 grams; 41.70 grams.

146. What weight of pure iron wire should be taken for the standardization of a 0.12 *N* solution of KMnO_4 if not more than 40.00 cc. of the solution are to be used?

147. In standardizing a KMnO_4 solution with pure $\text{Na}_2\text{C}_2\text{O}_4$ it was found that 0.2345 gram of the pure oxalate reacted with 34.50 cc. of the KMnO_4 . What is (a) the $\text{Na}_2\text{C}_2\text{O}_4$ -titre and (b) the normality of the KMnO_4 solution?

Ans. (a) 0.006797; (b) 0.1015 *N*.

148. The CaO-titre of a certain KMnO_4 solution is 0.002800. How many grams of $\text{K}_2\text{Cr}_2\text{O}_7$ must be taken to make a liter of potassium dichromate of the same strength?

149. Calculate the normality of a KMnO_4 solution from the following data: 28.56 cc. of $\text{KMnO}_4 \approx$ 32.15 cc. of FeSO_4 ; 26.23 cc. of $\text{K}_2\text{Cr}_2\text{O}_7 \approx$ 28.97 cc. of FeSO_4 ; 1 cc. of $\text{K}_2\text{Cr}_2\text{O}_7 =$ 0.005484 gram Fe.

Ans. 0.1001 *N*.

150. It was found by titration that 30.00 cc. of a 0.1067 *N* solution of $\text{K}_2\text{Cr}_2\text{O}_7$ required 32.60 cc. of a FeSO_4 solution; 30.50 cc. of a FeSO_4 solution required 32.00 cc. of a KMnO_4 solution; and 33.20 cc. of a KMnO_4 solution required 34.40 cc. of an $\text{H}_2\text{C}_2\text{O}_4$ solution. What was the normality of the $\text{H}_2\text{C}_2\text{O}_4$?

94 CALCULATIONS OF OXIDATION AND REDUCTION PROCESSES

151. In the determination of Ca in limestone, it was found that the CaC_2O_4 precipitate obtained from a 0.2500-gram sample required 45.65 cc. of a 0.1 *N* solution of KMnO_4 . Calculate the percentage of calcium in the sample.

Ans. 36.59 per cent.

152. Calculate the percentage of iron in a 0.5000-gram sample of iron ore if the titration required 40.25 cc. of 0.1250 *N* KMnO_4 and 2.50 cc. 0.1467 *N* FeSO_4 solution.

153. Calculate the percentage of chromium in a chromium ore if, after conversion of the chromium to the $\text{Cr}_2\text{O}_7^{=}$ form, the titration required 33.65 cc. of 0.2 *N* FeSO_4 . The sample of chromium ore weighed 0.6223 gram.

Ans. 18.75 per cent.

154. An ignited residue consisting of a mixture of Al_2O_3 and Fe_2O_3 which was obtained in a gravimetric analysis of limestone weighed 0.2500 gram. This was dissolved and the iron titrated with 0.1 *N* $\text{K}_2\text{Cr}_2\text{O}_7$ requiring 30.25 cc. Calculate the weight of Fe_2O_3 and of Al_2O_3 in the above residue.

155. How much water should be added to a liter of KMnO_4 , having an Fe-titre of 0.006000 which is to be used for oxidation in an acid medium in order to make the solution exactly 0.1 *N*?

Ans. 74 cc.

156. How much water should be added to 950.0 cc. of a solution whose Fe-titre is 0.005642 in order that it have an Fe-titre of 0.005584? What is the normality of the diluted solution?

157. What should be the normality of a KMnO_4 solution so that the volume used in a calcium determination should equal the percentage of CaO if the weight of sample used is 0.2500 gram?

Ans. 0.08916 *N*.

158. What should be the normality of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution so that the volume used in the titration of iron ores represents the percentage of iron in the sample if 0.7047-gram samples are taken for analysis?

159. A certain KMnO_4 solution has an Fe-titre of 0.005436. What weight of iron ore (assume to be pure Fe_2O_3) should be taken for analysis so that not more than 40.0 cc. of the KMnO_4 solution are required for the titration?

Ans. 0.3109 gram.

160. What weight sample of iron ore should be taken for analysis if the percentage of iron in the sample is approximately 50 per cent and not over 30.00 cc. of a dichromate solution, whose Fe-titre is 0.005584, are to be used?

OXIDATION-REDUCTION CALCULATIONS INVOLVING THE HALOGENS

The most extensive application of oxidimetric and reductimetric methods are those involving iodine, bromine and chlorine and their compounds. By suitable use of standard solutions of these and other reagents it is possible to determine no less than thirty of the chemical elements in hundreds of their compounds. For discussion, the methods will here be placed in three groups:

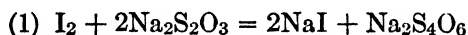
a. Direct titration with standard iodine, known as *iodimetric* methods.

b. Liberation of iodine and its titration with standard reducing reagents. These are the *iodometric* methods.

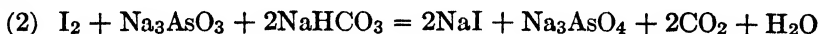
c. Use of potassium iodate, with and without potassium iodide; and potassium bromate, likewise with and without potassium bromide.

Iodimetric Methods. Many substances are quantitatively oxidized by iodine, using a starch solution as indicator. Commonly used in conjunction with the standard iodine solution are standard solutions of either sodium thiosulfate or sodium arsenite. The iodine is usually titrated directly into the solution of the sample whose constituent is to be oxidized, until the end point is reached, but in cases where the end point is overstepped or an excess of iodine is prescribed, back-titration with the standard reducing agent is employed.

The fundamental reactions between these reagents are:

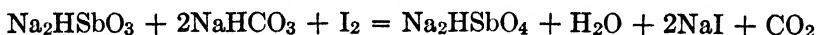


and

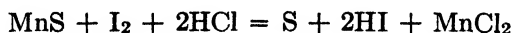


the sodium bicarbonate in reaction (2) being used to neutralize (buffer) the HI which otherwise would form and thus cause the reaction to reverse.

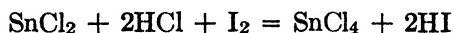
Iodimetric methods may be used in the determination of arsenites and thiosulfates, as already inferred. In analogous manner antimony may be determined, based on the reaction



Sulfides, especially in steel, are normally determined by oxidation with iodine, in the presence of acid:

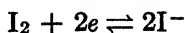


Tin, likewise:



Sulfites may be determined by using an excess of iodine with back titration with standard thiosulfate or arsenite.

Equivalent weights for normal solutions are readily derived from the equations given. Thus, for iodine, the reaction

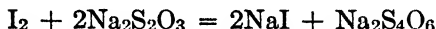


involves the gain of 2 electrons per molecule or a change in valence from 0 to -1 per atom, i.e., a decrease of 2 per molecule. The gram-equivalent weight is therefore one half of the molecular weight or the gram-atomic weight.

For $\text{Na}_2\text{S}_2\text{O}_3$, the reaction is



and the balanced molecular equation for the interaction between $\text{Na}_2\text{S}_2\text{O}_3$ and I_2 becomes



A liter of normal solution of the salt $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ calls for the gram-molecular weight, approximately 248.2 grams. Usually 0.1 *N* solutions of these reagents are employed in analysis.

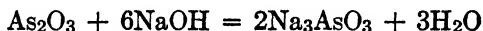
The gram-equivalent weight of Na_3AsO_3 or Na_2HAsO_3 , determined from reaction (2) already given, is one half of the gram-molecular weight, since the electron loss is 2:



or a change of valence of the arsenic atom from +3 to +5.

Example 1. What weight of pure As_2O_3 should be used for the preparation of a liter of 0.1 *N* Na_3AsO_3 solution?

When this is dissolved in NaOH , according to the reaction:



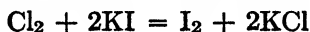
two molecules of Na_3AsO_3 are produced. Therefore $\frac{\text{As}_2\text{O}_3}{4}$ represents the equivalent. This is 49.5 grams and for one-tenth of an equivalent weight we need 4.95 grams.

Iodometric Methods. The principle upon which methods of this kind is based is the liberation of iodine from KI through the action of the constituent being determined and the subsequent titration of the liberated iodine with a standard sodium thiosulfate or sodium arsenite solution.

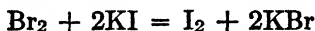
Oxidized form of Constituent + $\text{KI} \rightarrow$ Reduced form of Constituent + I_2 .

The fact that many substances are capable of oxidizing KI makes these methods of wide application.

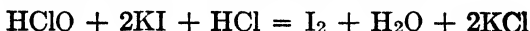
Free chlorine can thus be determined by the reaction:



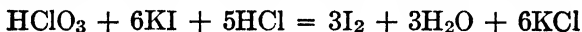
and the same is true for bromine:



Hypochlorites react in the following manner:

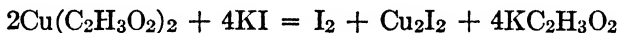


Chlorates liberate iodine in accordance with the reaction

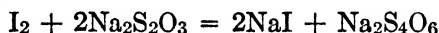


The same is true of bromates and iodates.

An important determination, frequently conducted by the beginning student in quantitative analysis, is that of copper. The essential reaction is:



and the liberated iodine is then titrated with a standard solution of sodium thiosulfate:

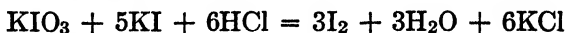


Example 2. A sample of copper ore weighing 0.5129 gram, properly treated with acids and then KI, liberated I_2 which was titrated with 39.86 cc. of 0.1032 *N* $\text{Na}_2\text{S}_2\text{O}_3$. What was the percentage of copper in the sample?

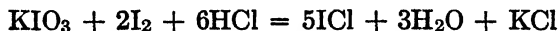
In the relation $2 \text{ Cu} : \text{I}_2 : 2\text{Na}_2\text{S}_2\text{O}_3$, the milliequivalent weight of copper is seen to be one-thousandth of the gram-atomic weight, that is, 0.06357. Therefore,

$$\frac{0.06357 \times 0.1032 \times 39.86}{0.5129} \times 100 = 50.98 \text{ per cent.}$$

Iodate and Bromate Methods. Potassium iodate and potassium bromate are strong oxidizing agents and can be used, alone, in the form of standard solutions, or, in admixture with KI or KBr, for the determination of many substances. With KIO_3 the final reduction product, in HCl medium, is iodine monochloride, ICl . When KIO_3 reacts with reducing agents the intermediate product is I_2 , which in turn reacts with the iodate to destroy the iodine. Titrations of this kind reach an end point when the blue color of the liberated iodine is discharged from a chloroform or carbon tetrachloride layer in the solution being titrated. The reactions by which ICl forms can be seen from the following, where KI is the reducing agent:

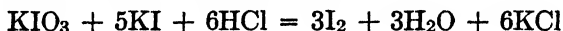


and



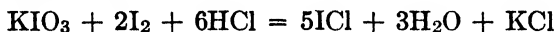
If the titration is stopped when the iodate has been reduced to

iodine, which can be accomplished in solutions of low acidity, the liberated iodine can be titrated with standard thiosulfate. Thus iodides can be oxidized to free iodine by the reaction

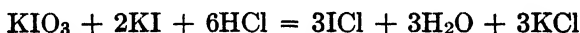


and determined in this way instead of effecting the formation of iodine monochloride.

From the equation

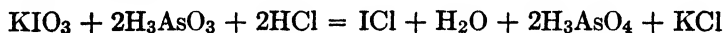


it is seen that iodine can be determined by direct titration with a standard solution of KIO_3 . Likewise, iodides, as for example, KI , can be determined by a similar titration



Among the many other substances that can be determined by titration with KIO_3 , with the formation of iodine monochloride, are arsenites, sulfites, thiosulfates, persulfates, tin, antimony and copper thiocyanate.

Example 3. What is the gram-equivalent weight of KIO_3 , when used in the reaction:

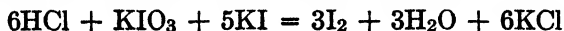


From the relation:



the iodine changes from a valence of 5 to 1, a total valence change of 4 or 4 electrons are needed; hence $\frac{\text{KIO}_3}{4}$ is the equivalent weight.

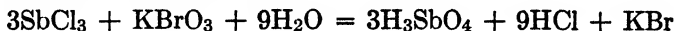
Certain substances, moreover, can be determined by use of a mixture of potassium iodate and potassium iodide, which react to liberate iodine. Iodine, in turn, can then be titrated with thiosulfate. The reaction just given for the determination of iodides:



may be used, as well, for the determination of strong acids like HCl and H_2SO_4 and by special adoption for H_3BO_3 and certain hydrolyzable salts.

Use of Potassium Bromate. Standardized solutions of potassium bromate, KBrO_3 , are frequently used in the determination of many substances. This oxidizing agent may be used either alone or along with KBr or KI in a variety of ways. The titration may be stopped

either when the bromate has been reduced to bromide or else reduced to free bromine. As examples of the first mode of procedure, the determination of such substances as the elements tin, iron, arsenic, titanium and antimony may be cited. In the case of antimony, the reaction proceeds in the following way.

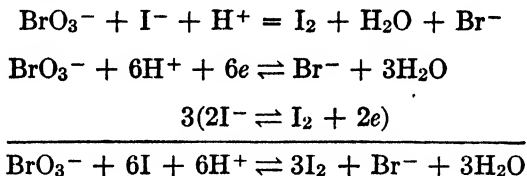


The reaction of KBrO_3 with iodides in an acid solution is an important one



Example 4. From the reaction just given derive the gram-equivalent weight of KBrO_3 .

The ionic reaction is:



The electron transfer is 6 (a change of valence from +5 to -1). Then $\frac{\text{KBrO}_3}{6}$, or one-sixth of the gram-molecular weight, is the gram-equivalent weight.

Further illustrations of uses, as well as suggested calculations, are illustrated in the accompanying problem set.

PROBLEM SET 9

CALCULATIONS INVOLVING HALOGENS IN VOLUMETRIC OXIDATION-REDUCTION PROCESSES

161. What weights of pure (a) I_2 , (b) As_2O_3 and (c) $\text{Na}_2\text{S}_2\text{O}_3$ are required for liter quantities of 0.05 *N* solutions of these reagents, the As_2O_3 being converted by NaOH into Na_3AsO_3 ? Calculate the I_2 -titres, the As_2O_3 -titres and the Cu -titres of these solutions.

Ans. 6.347; 2.473; 7.905; 0.00635; 0.002473; 0.003179.

162. If 0.2500 gram of pure As_2O_3 was required for the standardization of an iodine solution using 28.65 cc. of the iodine and 1.50 cc. of Na_3AsO_3 (1 cc. $\text{I}_2 \approx 1.20$ cc. Na_3AsO_3), what are (a) the As -titres of the two solutions and (b) their normalities?

163. What would be a suitable weight of pure re-sublimed iodine to use (a) for the standardization of a 0.01 *N* $\text{Na}_2\text{S}_2\text{O}_3$ solution? (b) for the standardization of a 0.01 *N* Na_3AsO_3 solution in each case using 40 cc.?

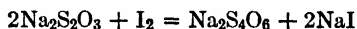
Ans. 0.0508 gram; 0.0508 gram.

100 CALCULATIONS OF OXIDATION AND REDUCTION PROCESSES

164. What weight of As_2O_3 would you take for the preparation of a liter of 0.5 *N* sodium arsenite solution ($\text{As}_2\text{O}_3 + 6\text{NaOH} = 2\text{Na}_3\text{AsO}_3 + 3\text{H}_2\text{O}$) to be used in conjunction with iodine according to the following reaction:



How much $\text{Na}_2\text{S}_2\text{O}_3$ would be required for a liter of 0.5 *N* solution according to the following reaction:



For the preparation of a 0.5 *N* solution of I_2 in the above reactions, how much I_2 would be required?

165. Calculate the percentage of As_2O_3 in a sample of an arsenical preparation if a 0.5000-gram sample requires 34.68 cc. of iodine solution which contained 0.01250 gram of iodine per cubic centimeter. *Ans.* 33.80 per cent.

166. What is the purity of a sample of disodium arsenite Na_2HAsO_3 if 36.42 cc. of a 0.1 *N* solution of I_2 are used in titrating a 0.3500-gram sample?

167. What is the percentage of As_2O_3 in a sample of disodium arsenite, Na_2HAsO_3 , if 36.54 cc. of 0.1 *N* I_2 are used in titrating a 0.2000-gram sample? If the material is listed as sodium metarsenite, NaAsO_2 , what will be the percentage of As_2O_3 using the same data? *Ans.* 90.38 per cent.

168. To make an iodine solution exactly 0.1 *N* how much water should be added to 850 cc., the iodine solution being 0.1562 *N*?

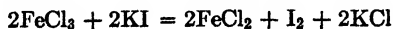
169. In order that each cubic centimeter of a $\text{Na}_2\text{S}_2\text{O}_3$ should represent 1 per cent of Cu, what should be its normality if a 2.0000-gram sample is analyzed?

Ans. 0.3146 *N*.

170. A 3.0000-gram sample of steel was treated with HCl, the evolved H_2S precipitated as CdS and the CdS dissolved in an acidified solution containing 50.00 cc. of 0.01 *N* iodine solution. The excess iodine was titrated with 46.52 cc. of 0.01 *N* Na_3AsO_3 solution. Calculate the percentage of sulfur in the steel.

171. Calculate the percentage of antimony in a sample of antimony ore from the following data: The determination required 32.65 cc. of iodine, which in standardizing required 0.1478 gram of pure As_2O_3 for 30.00 cc. of iodine. The weight of sample was 0.9637 gram. *Ans.* 12.6 per cent.

172. The iodine liberated from KI by FeCl_3 in a hydrochloric-acid solution, by the reaction:

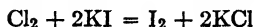


may be used, with certain precautions, as the basis for the determination of iron. If the iodine liberated in the above reaction requires 33.00 cc. of 0.1 *N* sodium thio-sulfate solution, what weight of Fe was represented?

✓ **173.** The ore, pyrolusite (impure MnO_2), was at one time extensively used as a source of chlorine, which is evolved when the ore is treated with HCl:

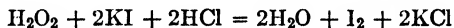


If, in evaluating a sample of this ore, the Cl_2 is passed into KI solution, where the reaction



takes place, and the free iodine is titrated with 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ solution, what is the percentage of available chlorine, the weight of sample being 0.265 gram and the volume of $\text{Na}_2\text{S}_2\text{O}_3$ being 18.72 cc.? *Ans.* 25.05.

174. If a 10-cc. sample of hydrogen peroxide requires 27.65 cc. of a 0.4975 *N* solution of $\text{Na}_2\text{S}_2\text{O}_3$ for the reduction of the iodine liberated in the reaction



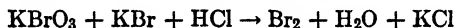
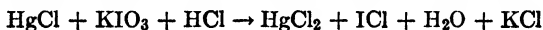
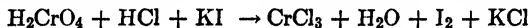
what is the percentage of H_2O_2 in the sample?

175. A sample of a chromium ore was oxidized to $\text{Na}_2\text{Cr}_2\text{O}_7$ by a sodium peroxide fusion, and this, after removal of iron and other impurities, treated with HCl to convert it into $\text{Na}_2\text{Cr}_2\text{O}_7$. An excess of potassium iodide was then added, liberating iodine in accordance with the reaction



The liberated iodine was titrated with 38.65 cc. of 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ solution. If the weight of sample was 1.2230 grams what was the percentage of chromium in the sample? *Ans.* 5.48 per cent.

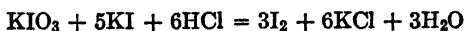
✓ 176. Balance the following equations showing the electrons lost and gained:



177. Balance the following equations, with half-cell reactions showing the electron transfers:



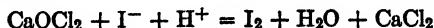
178. From the reaction



calculate the gram-equivalent weight of KIO_3 .

✓ 179. How much I_2 will be liberated from 35.67 cc. of 0.1482 *N* $\text{K}_2\text{Cr}_2\text{O}_7$ solution when treated with KI and HCl? *Ans.* 0.6709.

✓ 180. Calculate the percentage of CaOCl_2 in a 0.2500-gram sample of bleaching powder which was treated with excess KI and acidified with HCl, and the iodine liberated in the reaction



was titrated with 30 cc. of 0.05 *N* $\text{Na}_2\text{S}_2\text{O}_3$ solution.

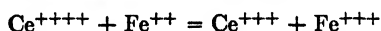
FURTHER APPLICATIONS OF OXIDATION AND REDUCTION REACTIONS TO VOLUMETRIC PROCEDURES

In the following set of problems (Problem Set 10) are presented additional problems which further illustrate the calculations and methods of analysis in this important field of analytical chemistry. With the previous practice the student has had in calculations involving the preparation and standardization of solutions, titres and normalities and general titration procedure, it is deemed unnecessary to discuss further such calculations or to offer additional illustrative examples. It has been the aim to present, in this final set, problems of somewhat greater difficulty and more complex nature in order to test the student's full grasp of volumetric calculations.

PROBLEM SET 10

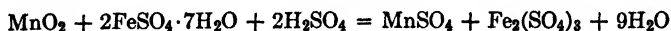
ADDITIONAL OXIDATION-REDUCTION CALCULATIONS

181. Ceric sulfate, procurable as the double ceric ammonium sulfate, $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, is coming into use as a standard oxidizing reagent. If 35.00 cc. of a 0.1 *N* solution of this reagent are required to oxidize the iron in a 1-gram sample of iron ore, what is the percentage of iron in the sample? The ionic reaction is:



Ans. 19.54 per cent.

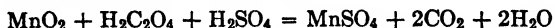
182. The manganese in a 1-gram sample of a ferro alloy was oxidized to MnO_2 by means of KClO_4 . The MnO_2 was dissolved in 0.3000 gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$:



The excess of ferrous sulfate was titrated with standard KMnO_4 , whose Fe-titre was 0.003268.

$2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 + 10\text{FeSO}_4 = 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}$
 requiring 16.56 cc. Calculate the percentage of manganese in the alloy.

183. A sample of pyrolusite (impure MnO_2) weighing 0.4000 gram was treated with 50.00 cc. of 0.5 *N* oxalic acid solution:

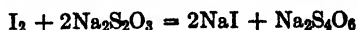


The excess of oxalic acid was then titrated with 0.5 *N* KMnO_4 requiring 35.50 cc. Calculate the percentage purity of the sample. *Ans.* 78.79 per cent.

184. A student employed a standard solution of KMnO_4 (Fe-titre = 0.005500) as a means of standardizing a $\text{Na}_2\text{S}_2\text{O}_3$ solution which he wished to use in a copper determination. He treated 35.00 cc. of the permanganate solution with an excess of KI

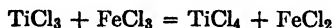


and titrated the liberated I_2 with 37.82 cc. of the $\text{Na}_2\text{S}_2\text{O}_3$ solution:



Calculate the Cu-titre of the $\text{Na}_2\text{S}_2\text{O}_3$.

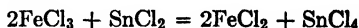
185. Titanous chloride is sometimes used, with certain precautions, as an effective standard reducing reagent. It may be used particularly in the determination of ferric iron:



How much TiCl_3 would be required for the preparation of a liter of 0.1 *N* solution? How much pure iron would be required to standardize such a solution, if it were planned to use 40.00 cc. in the standardization titration?

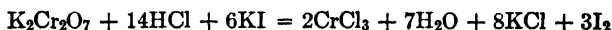
Ans. 15.43 grams; 0.2234 gram.

186. If a freshly prepared standard solution of SnCl_2 is used to titrate the iron in a sample of FeCl_3 , by reduction

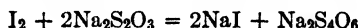


what is the weight of iron in the sample, 27.32 cc. of the SnCl_2 being required, the solution being 0.5 *N*?

187. In standardizing a $\text{Na}_2\text{S}_2\text{O}_3$ solution, by titrating the I_2 liberated from KI by the action of a standardized solution of $\text{K}_2\text{Cr}_2\text{O}_7$, in accordance with the following reactions:



and



the following data were secured: volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used = 32.35 cc.; normality of $\text{K}_2\text{Cr}_2\text{O}_7$ solution = 0.1050; volume of $\text{Na}_2\text{S}_2\text{O}_3$ used = 35.00 cc. Calculate the normality of the $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Ans. 0.09706 *N*.

188. If 50.00 cc. of a 0.1 *N* KMnO_4 solution acidified with sulfuric acid are placed in a beaker and from a burette are added 35.75 cc. of HNO_2 , what is the weight of pure HNO_2 in the sample? The reaction that takes place is:



189. Hydrogen peroxide reacts with KMnO_4 in an acidified solution in accordance with the following reaction:



Calculate the gram-milliequivalent weight of hydrogen peroxide. If 1 cc. of the commercial H_2O_2 after dilution and acidification is titrated with 20.50 cc. of a 0.1162 *N* KMnO_4 solution, what is the percentage of H_2O_2 in the sample?

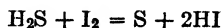
Ans. 0.01701; 4.05 per cent.

190. If you were to mix 30.00 cc. of a 0.09762 *N* solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and 20.00 cc. of a 0.1075 *N* solution of KMnO_4 and then acidified and treated the mixture with an excess of KI , what volume of 0.1 *N* Na_3AsO_3 would be required to titrate the liberated iodine? The reactions taking place are:



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191. In determining the sulfur in a sample of steel, by treatment with HCl, precipitation of the evolved H_2S as CdS , the dissolving of this in HCl and titration with 0.05 *N* iodine, according to the reaction



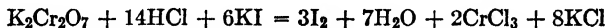
what weight of steel sample should be taken so that each cubic centimeter of iodine will equal 1 per cent of sulfur? *Ans.* 0.08015.

192. A 0.2500-gram sample of ferro-manganese containing 75.00 per cent of manganese was titrated with 0.1 *N* KMnO_4 according to the reaction



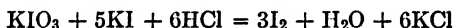
How many cubic centimeters were required?

193. A $\text{Na}_2\text{S}_2\text{O}_3$ solution was standardized by treating a 1.5678-gram sample of steel containing 0.80 per cent Cr with an oxidizing agent to convert the Cr into $\text{K}_2\text{Cr}_2\text{O}_7$, and then titrating the iodine liberated from KI in accordance with the reaction



with the thiosulfate solution, using 29.27 cc. of $\text{Na}_2\text{S}_2\text{O}_3$. What was the normality of the $\text{Na}_2\text{S}_2\text{O}_3$? *Ans.* 0.02471.

194. A mixture of KIO_3 and KI containing 0.3000 gram of pure KIO_3 was treated with HCl and the I_2 liberated in the reaction

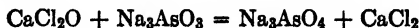


titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution, using 37.62 cc. What was the normality of the $\text{Na}_2\text{S}_2\text{O}_3$ solution?

195. Forty cubic centimeters of KMnO_4 are equivalent to 35.00 cc. of a $\text{K}_2\text{Cr}_2\text{O}_7$ solution, of which 1 cc. will liberate 0.02687 gram of I_2 from KI. What is the normality of the KMnO_4 solution? *Ans.* 0.1852 *N*.

196. A 0.5-gram sample of iron ore was titrated with 0.1 *N* $\text{K}_2\text{Cr}_2\text{O}_7$. The end point was overstepped when 52.00 cc. of the reagent had been added. On adding 0.8267 gram of Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, the titration was continued, using an additional 5.75 cc. of the dichromate solution. Calculate the percentage of iron in the sample.

197. In determining the available chlorine in bleaching powder, 2.5 grams of the sample were ground to a paste with water, dissolved and diluted to 500 cc. An aliquot portion of 50 cc. required 25 cc. of a 0.1 *N* Na_3AsO_3 solution. The reaction is



Calculate the percentage of available chlorine in the sample.

Ans. 35.46 per cent.

198. Free chlorine may be determined by its action on KI



titrating the liberated iodine with standard thiosulfate solution. If 50 cc. of

chlorine water, when treated with KI and titrated with 0.1250 *N* Na₂S₂O₃ required 30 cc., what was the strength of the sample in terms of Cl₂ per cubic centimeter?

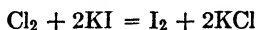
199. A sample of lead paint was dissolved, the lead precipitated as PbCrO₄, dissolved in acid and treated with KI. The liberated iodine was titrated with 0.1 *N* Na₂S₂O₃, requiring 36.50 cc. What was the weight of lead in the paint?

Ans. 0.2521.

200. A sample of MnO₂ ore was treated with HCl, liberating free chlorine



and the chlorine passed into KI solution



The iodine was titrated with 0.1 *N* Na₂S₂O₃ solution, requiring 40.00 cc. for a 0.5-gram sample of the ore. Calculate the purity of the ore.

PART III

THE CALCULATIONS OF GRAVIMETRIC ANALYSIS

CHAPTER VII

GENERAL CONSIDERATIONS OF GRAVIMETRIC ANALYSIS

THE CALCULATION AND USE OF CHEMICAL FACTORS

The amount of constituent in a sample of material is determined most generally by one of two chemical methods: Either the amount of reagent required for the reaction is measured, as in a titration process, or else the amount of product formed in the reaction is weighed. The latter procedure embraces the gravimetric methods of determination. Most of the gravimetric methods depend upon reactions in which a precipitate is formed. To meet the exacting requirements of a precise gravimetric method of determination it is important that (1) the reaction selected must run to practical completion, (2) the precipitate must possess the physical qualities which enable it to be separated from the solution by filtration and purified from contaminating substances and (3) the dried or ignited product must have a definite, known chemical composition. In short, if a pure product, containing the constituent in question, can be separated and weighed, we have the basis for an accurate method of quantitative determination.

The steps involved in carrying out the technique of gravimetric analysis may be briefly summarized as follows:

1. The weighing of suitable amounts of the properly prepared sample.
2. The preparation and bringing to constant weight of crucibles in which the purified precipitate is later weighed.
3. The preparation of the necessary reagents, especially the precipitating agent.
4. The dissolving of the sample, separation of interfering constituents if necessary, bringing the solution to the proper acidity, basicity or state of oxidation and then adding an excess of precipitating reagent.
5. Filtering and washing the precipitate until free from impurities.

6. Drying or igniting and finally weighing the crucibles which now contain the precipitate.

In keeping with these manipulative steps are the computations of gravimetric analysis. These are here briefly enumerated and then discussed at greater length.

1. Calculation of weight of sample to be taken for analysis.
2. Calculation of solute for the preparation of reagents.
3. Calculation of the volume of precipitating reagent required.
4. Calculation of the amount, usually expressed as a percentage, of the constituent in the sample.
5. Certain equilibrium calculations based on ionization and solubility data, by which the solution is brought to a correct condition and by which the theoretical error of the method can be estimated.

The Theory of Gravimetric Analysis. Before discussing these calculations in detail it is well to present the fundamental theory of gravimetric analysis. The theory of reactions, resting fundamentally on the Law of Combining Weights and the Law of Chemical Equilibrium, finds in the methods of quantitative analysis very important applications. Any reaction which is to serve as the basis of a quantitative method of determination must run practically to completion. This means that when final equilibrium is reached the concentration of the ion whose determination is sought must be low enough not to affect seriously the accuracy of the analysis. The Law of Chemical Equilibrium enables us to calculate the amount of constituent un-acted upon; in the case of a gravimetric precipitation method, an equilibrium calculation, as shown later, will give the amount of constituent unprecipitated.

On the other hand, the Law of Combining Weights enables us to calculate the amount of constituent contained in a definite weighed amount of the purified product of the reaction. If, then, the reaction between the precipitating agent and the constituent to be determined has been allowed to proceed so far to completion that only negligible amounts of constituent remain unprecipitated, and the precipitate is carefully purified, filtered and dried in a pure form or, if necessary, converted by ignition to a definite compound of known chemical composition and the dried or ignited precipitate weighed, the amount of constituent in the final weighed product can readily be calculated. The calculation itself is based on a proportionality between actual weights and the molecular or atomic weights involved. The relationship assumes the form of a direct proportion:

Mol. or at. wt. of constituent: Mol. wt. of product = Actual weight of constituent: Actual weight of product.

Or, expressed in the form of ratios:

$$\frac{\text{Mol. or at. wt. of constituent}}{\text{Mol. wt. of product}} = \frac{\text{Actual weight of constituent}}{\text{Actual weight of product}}$$

Here the Law of Combining Weights is specifically applied to the calculation of the weight of constituent which has entered into chemical combination in the final weighed product of the reaction. Thus, if we wish to know how much silver is contained in a given weight of AgCl, we can easily solve for x in the equation:

$$\frac{\text{Atomic weight of Ag}}{\text{Molecular weight of AgCl}} = \frac{\text{Weight of Ag}(x)}{\text{Weight of AgCl}}$$

and if the AgCl is that obtained by precipitating the silver in a sample of silver alloy, we then know the amount of silver in the alloy.

This is equivalent to finding how much Ag has reacted to produce the given weight of AgCl. That is to say, we have applied the Law of Combining Weights to the reaction between silver and chloride.

The Law of Combining Weights, just applied specifically to the calculation of the amount of constituent contained in a weighed amount of reaction product, is of course, of much wider application. It enables us not only to calculate the proportion of constituents in pure compounds but, also the amount of product formed in a reaction, as well as the amount of reagent required. In short, the amounts of the components in a reaction are precisely defined by this most fundamental of all chemical laws, and by means of it the proportions by which substances react with each other become known.

Gravimetric Chemical Factors. When this proportionality is expressed in the form of ratios, as, for instance,

$$\frac{\text{At. wt. of Ag (107.88)}}{\text{Mol. wt. of AgCl (143.34)}} = \frac{\text{Weight of Ag}}{\text{Weight of AgCl}}$$

the ratio of the atomic weight of silver to the molecular weight of AgCl is a constant. It means that in 143.34 parts by weight of AgCl there are 107.9 parts by weight of Ag, or, since

$$\frac{\text{At. wt. Ag}}{\text{Mol. wt. AgCl}} = \frac{107.88}{143.34} = 0.7526$$

the amount of the Ag in AgCl is 0.7526 of the whole. This ratio is known as a *chemical factor*, and the number given is the chemical factor repre-

sending the proportional amount of Ag in AgCl. It can be interpreted as meaning the fractional part of Ag in unit quantity of AgCl, for, by stoichiometric relation:

$$\frac{\text{Ag}}{\text{AgCl}} = \frac{x \text{ gram of Ag}}{1 \text{ gram of AgCl}}$$

$$\frac{107.88}{143.34} \times 1 = x$$

$$x = 0.7526 \text{ gram}$$

Or, on the basis of a percentage designation, the parts of Ag contained in 100 parts of AgCl resolve into:

$$\frac{\text{Ag}}{\text{AgCl}} = \frac{x \text{ parts of Ag}}{100 \text{ parts of AgCl}}$$

$$\frac{107.88}{143.34} \times 100 = x$$

$$x = 75.26 \text{ parts per hundred parts (per centum, per cent)}$$

In other words, pure AgCl contains 75.26 per cent of silver.

In a more general way, the factor may be used to convert a given weight of AgCl into its corresponding weight of Ag. For example, in 0.2000 gram of AgCl, the amount of Ag might be calculated by the direct proportion,

$$\frac{\text{Ag}(107.88)}{\text{AgCl}(143.34)} = \frac{x}{0.2000}$$

But, since the ratio of Ag to AgCl is known by the chemical factor to be 0.7526, it is simpler merely to multiply the weight of AgCl by this conversion factor.

$$0.2000 \times 0.7526 = 0.1505$$

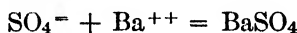
From this viewpoint, chemical factors are *conversion factors*. Since a direct weight relationship is involved and, moreover, because such factors are extensively used in gravimetric analysis and particularly to calculate the amount of constituent contained in a pure, ignited weighed compound, these factors are frequently referred to as *gravimetric factors*. Tables of gravimetric factors are found in many textbooks of quantitative analysis and in most handbooks of chemistry.

Calculation of Chemical Factors. The actual computation of gravimetric factors, as already illustrated in the case of the ratio of Ag to AgCl, is in itself a simple matter. The first requirement is that the chemical equation, whether real or hypothetical, be written and properly bal-

anced, or, at least, that the constituent concerned, common to numerator and denominator, be correctly involved. Then it remains to use the atomic and molecular weights with proper coefficients. It is important in setting up the ratio that the constituent or substance desired appear as numerator and the given or weighed substance be in the denominator.

Example 1. Calculate the factor required to convert BaSO_4 to SO_4 .

The chemical equation is



The desired ratio is $\frac{\text{SO}_4}{\text{BaSO}_4}$ and therefore

$$\frac{\text{SO}_4}{\text{BaSO}_4} = \frac{96.06}{233.42} = 0.4115$$

Example 2. What is the factor required to convert Fe_2O_3 to Fe?

Since in Fe_2O_3 there are 2Fe, the ratio is 2 atoms of Fe to 1 molecule of Fe_2O_3 :

$$\frac{2\text{Fe}}{\text{Fe}_2\text{O}_3} = \frac{2 \times 55.84}{(2 \times 55.84) + (3 \times 16)} = 0.6994$$

The Use of Chemical Factors. Chemical factors are used to relate the weight of one substance to another and may conveniently be employed in calculating such quantities as the weight of reagent required in a reaction, the weight of product obtained or the amount of constituent contained in a given weight of pure compound.

Example 3. What weight of Na_2CO_3 will react with 0.1685 gram of HCl?

The reaction is



The chemical factor is

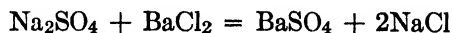
$$\frac{\text{Na}_2\text{CO}_3}{2\text{HCl}} = \frac{105.99}{2 \times 36.46} = 1.4535$$

This may be interpreted to mean that 1.4535 parts of Na_2CO_3 are equivalent to 1 part of HCl, or that 1 gram of HCl will react with 1.4535 grams of Na_2CO_3 . Therefore

$$0.1685 \times 1.4535 = 0.2449 \text{ gram}$$

Example 4. What weight of BaSO_4 will be obtained from 0.2500 gram of pure Na_2SO_4 by precipitation with BaCl_2 ?

The reaction is



The chemical factor is

$$\frac{\text{BaSO}_4}{\text{Na}_2\text{SO}_4} = \frac{233.42}{142.058} = 1.6432$$

Therefore, to convert 0.2500 gram of Na_2SO_4 into its equivalent of BaSO_4 , it is merely necessary to multiply the weight of Na_2SO_4 by the chemical factor.

$$0.2500 \times 1.6432 = 0.4108 \text{ gram}$$

Example 5. How much iron is contained in 0.2591 gram of ignited Fe_2O_3 ?

The chemical factor, already obtained in Example 2, is

$$\frac{2\text{Fe}}{\text{Fe}_2\text{O}_3} = 0.6994$$

Then

$$0.2591 \times 0.6994 = 0.1812 \text{ gram}$$

Calculation of the Percentage of Constituent from Gravimetric Data. In gravimetric analysis, the constituent undergoing determination is isolated as an insoluble precipitate, in most cases, and then dried or ignited and weighed in the form of a pure compound of definite, known chemical composition. We can then, by direct proportion or by use of the appropriate chemical factor, calculate the weight of constituent in the weighed product. If more than one similar calculation is to be made, as in duplicate or triplicate analyses, it is naturally advantageous to use the chemical factor; otherwise, one can, of course, calculate the weight of constituent by direct proportion. In either case, the weight of constituent sought, divided by the weight of sample, will give the ratio of pure constituent to impure sample and, to express this as a percentage (per centum, or parts per 100), this value is multiplied by 100.

In using the chemical factor, the calculation reduces itself to the fundamental formula:

$$\frac{\text{Weight of precipitate} \times \text{Chemical factor}}{\text{Weight of sample}} \times 100 = \text{per cent}$$

Example 6. What is the percentage of sulfate in a sample of impure Na_2SO_4 , if 0.5000 gram of the sample yields, upon reaction with BaCl_2 , a precipitate of BaSO_4 weighing 0.8112 gram?

The weight of SO_4 corresponding to 0.8112 is found by proportion thus:

$$\begin{array}{ccc} \text{SO}_4 : \text{BaSO}_4 = x : 0.8112 \\ (96.06) & (233.42) \end{array}$$

where x is the weight of SO_4 contained in this weight of BaSO_4 , and by calculation equals 0.3338 gram.

The weight may also be found by multiplying the chemical factor for SO_4 in BaSO_4 by the weight of BaSO_4 . The factor for SO_4 in BaSO_4 , $\frac{\text{Mol. weight of SO}_4}{\text{Mol. weight of BaSO}_4}$, is 0.4116. If to this ratio is assigned a definite weight as, for instance, the fractional part of 1 gram, the value 0.4116 represents the weight of SO_4 contained in 1 gram of BaSO_4 . Since we have 0.8112 gram of BaSO_4 , the weight of SO_4 is 0.8112×0.4116 , or 0.3338 gram. It will be observed when these two methods are examined that, once the chemical factor is known, the subsequent operation is a single multiplication. The rule to be followed then, when there are two or more sets of data involving the same relationship, as for example, in using the data in duplicate or triplicate analyses of the same material, is always to apply the chemical factor. No particular advantage is derived by applying the factor to a single set of data.

The amount of SO_4 contained in the weight of original sample expressed as a decimal is then found by dividing the former by the latter, $0.3338 \div 0.5000 = 0.6676$; and multiplying this by 100 gives 66.76 per cent (parts per hundred).

In general, calculations of percentage composition can be made by use of the general equation:

$$\frac{\text{Weight of precipitate} \times \text{Chemical factor}}{\text{Weight of sample}} \times 100 = \text{per cent}$$

PROBLEM SET 11

CALCULATION OF FACTORS AND PERCENTAGES IN GRAVIMETRIC ANALYSIS

201. Calculate the number of grams of the specified constituent which are contained in 1.0000 gram of the following compounds.

Desired constituent		
(a) BaSO_4	SO_4	Ans. (a) 0.4115.
(b) AgCl	Cl	(b) 0.2474.
(c) Fe_2O_3	Fe	(c) 0.6994.
(d) CaO	Ca	(d) 0.7147.
(e) $\text{Mg}_2\text{P}_2\text{O}_7$	Mg	(e) 0.2187.

202. Calculate the number of grams of the specified constituent contained in 0.3487 gram of BaSO_4 .

Constituent

- (a) Ba
- (b) S
- (c) O
- (d) SO_4

203. If 0.5382 gram of Na_2SO_4 is allowed to react with BaCl_2 , what weight of BaCl_2 will be required? What weight of BaSO_4 will be produced? If 0.5872 gram of BaSO_4 is produced in a reaction with Na_2SO_4 , what weight of Na_2SO_4 was involved?

Ans. 0.7891; 0.8844; 0.3574.

204. Calculate the chemical factors corresponding to

- (a) Ba in BaSO_4
- (b) Cl in AgCl
- (c) Fe in Fe_2O_3
- (d) MgO in $\text{Mg}_2\text{P}_2\text{O}_7$
- (e) CO_2 in CaCO_3

205. Calculate the logarithms of the factors for

- | | |
|--|------------------------------|
| (a) Ba in BaSO_4 | <i>Ans.</i> (a) 9.7698 — 10. |
| (b) Fe in Fe_2O_3 | (b) 9.8442 — 10. |
| (c) Ag in AgCl | (c) 9.8766 — 10. |
| (d) Mg in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ | (d) 8.9961 — 10. |
| (e) Ni in $\text{Ni}(\text{CH}_3)_4(\text{CNO})_4\text{H}_2$ | (e) 9.3079 — 10. |

206. When the following precipitates are ignited, the ignited products, specified below, are obtained. Write the balanced equations for the ignition. Calculate the factors called for below by writing the necessary balanced equations.

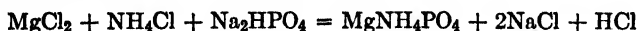
Precipitate	Ignited Product	Constituent sought
(a) CaC_2O_4	CaO	Ca
(b) $\text{Fe}(\text{OH})_3$	Fe_2O_3	Fe
(c) MgNH_4PO_4	$\text{Mg}_2\text{P}_2\text{O}_7$	P
(d) $(\text{NH}_4)_2\text{PtCl}_6$	Pt	N

207. By use of the appropriate chemical factor convert 1 gram of Fe to (a) Fe_2O_3 , (b) Fe_3O_4 , (c) FeO .

Ans. (a) 1.4298; (b) 1.3820; (c) 1.2865.

208. What weight of AgCl will be obtained from 0.2387-gram weight of impure NaCl containing 92.30 per cent pure NaCl ?

209. In the reaction



- (a) how much MgCl_2 will be required to produce 0.3148 gram of MgNH_4PO_4 ?
- (b) how much Na_2HPO_4 will be required to produce the same weight of MgNH_4PO_4 ?

Ans. (a) 0.2182; (b) 0.3255.

210. Calculate the percentage of (a) Fe (b) SO_4 in $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$. If a 0.3000-gram sample of the impure salt yielded upon precipitation of the SO_4 as BaSO_4 0.0750 gram, what is percentage (c) of SO_4 in the sample, (d) percentage purity of the sample?

211. If a 0.5000-gram sample of iron ore (impure Fe_2O_3) were dissolved in acid, and the iron precipitated as $\text{Fe}(\text{OH})_3$ and ignited to Fe_2O_3 yielded 0.2698 gram of Fe_2O_3 , how much pure Fe was contained in the sample?

Ans. 37.74 per cent Fe.

212. Calculate the percentage of Cl in a mixture consisting of equal parts by weight of pure NaCl and KCl. Do the same for an equimolecular mixture of NaCl and KCl.

213. A 0.5000-gram of limestone, when analyzed for magnesium, by precipitating MgNH_4PO_4 and igniting this to $\text{Mg}_2\text{P}_2\text{O}_7$, yielded 0.0315 gram of the ignited product. Calculate the percentage of MgO. If a 0.5000-gram sample of fertilizer yielded 0.1175 gram of $\text{Mg}_2\text{P}_2\text{O}_7$, what is the percentage of P_2O_5 ?

Ans. 2.28 per cent MgO; 14.98 per cent P_2O_5 .

214. Duplicate determinations of the SO_4 in a sample of material gave 0.6854 gram and 0.6846 gram of BaSO_4 , using 0.7000-gram samples. Calculate (a) percentage of SO_4 obtained in each determination, (b) the precision of the analysis in parts per thousand.

215. If a 0.2500-gram sample of impure sodium chloride yielded 0.5800 gram of pure AgCl , what was (a) the percentage of chloride in the sample, (b) the percentage purity of the sample?

Ans. (a) 57.40 per cent; (b) 94.60 per cent.

216. A limestone sample on analysis was found to contain 95 per cent of a mixture of CaCO_3 and MgCO_3 . A separate analysis for magnesium when recalculated to the oxide gave 8.00 per cent MgO. Calculate the percentage of CO_2 in the sample.

217. A sample of NaH_2PO_4 weighing 0.3756 gram yielded an ignited residue of 0.2790 gram of $\text{Mg}_2\text{P}_2\text{O}_7$ when treated with magnesia mixture and converted into the pyrophosphate. What was the percentage of PO_4 in the sample?

Ans. 63.39 per cent.

218. Calculate the percentage composition of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

219. In a duplicate determination of chloride by precipitating and weighing the AgCl , a chemist reported 35.67 and 35.82 per cent of Cl. What was the accuracy of his results? If the true percentage was 35.72, what was his percentage error in each determination?

Ans. 1.4 parts/1000.

2.8 parts/1000.

Percentage error = 0.139, or 0.14 per cent.

Percentage error = 0.279, or 0.28 per cent.

220. If a sample of material is known to contain 50.00 per cent of a certain constituent and an error of 0.2 of 1 per cent is permissible, what analytical results can be reported?

CALCULATIONS OF REAGENTS USED IN GRAVIMETRIC ANALYSIS

From the equation for any chemical reaction, the reacting proportions can readily be calculated, either by direct, stoichiometric proportion, or, more simply, by use of the chemical factor. Thus, in a precipitation reaction, the weight of precipitant (as well as the weight of precipitate) can be ascertained. When applied to the precipitation of a constituent in a sample of material, the approximate amount of constituent should be known; otherwise the calculation is based on the assumption that the sample is pure.

Strength of Precipitating Reagent. Before the amount of precipitating agent can be computed, the strength of the reagent must be approximately known. The strength of many precipitating agents employed in gravimetric analysis is expressed on an empirical basis (see Chapter II, page 17), usually in grams per liter, as best suited for the particular purpose intended. It is most convenient to convert the quantity of solute per liter into the value per cubic centimeter, and, if necessary, express this value in terms of the constituent being precipitated. To illustrate, suppose experience shows that a AgNO_3 solution containing 20 grams of AgNO_3 per liter is best suited for the precipitation of chloride as AgCl . Such a solution would contain 0.020 gram of AgNO_3 per cubic centimeter. The weight of Cl brought into reaction by 1 cc. of AgNO_3 would therefore be, using the chemical factor of $\frac{\text{Cl}}{\text{AgNO}_3} = 0.2087$,

$$0.020 \times 0.2087 = 0.004174 \text{ gram Cl per cubic centimeter}$$

The weight per cubic centimeter is known as a *titre* value. In the illustration just given the value 0.020 is the AgNO_3 -titre of the AgNO_3 solution and the value 0.004174 is the Cl-titre of the AgNO_3 solution. Titres are used extensively in both gravimetric and volumetric analysis.

Example 1. Calculate the SO_4 -titre of a solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, containing 15.0 grams of the solute per liter.

The $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ -titre is 0.0150 gram since this is the weight of solute per cubic centimeter. We have therefore

$$\frac{\text{SO}_4}{\text{BaCl}_2 \cdot 2\text{H}_2\text{O}} = \frac{96.06}{244.31} = \frac{x}{0.0150}$$

$$x = 0.00589 \text{ gram per cubic centimeter}$$

or, simply, by chemical factor

$$0.3932 \times 0.0150 = 0.00589 \text{ gram per cubic centimeter}$$

In the preparation of solutions of HCl and H₂SO₄, used as precipitating reagents, in the determination of silver and barium, respectively, reference must be made to the specific-gravity tables for these acids, since their strength is indicated in terms of percentage of pure solute corresponding to the specific gravity of the solution. The calculations involved in preparation of solutions of this type, by dilution, have already been discussed in Chapter II. When they are precipitating agents the appropriate titre designation is the most useful.

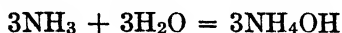
The use of ammonium-hydroxide solution as precipitating reagent for iron, aluminum and several other elements which are quantitatively precipitated as the hydroxide calls for special precaution in the designation of its strength. Instead of percentage of NH₄OH, the specific-gravity table gives the equivalent in terms of NH₃. In the precipitation of Fe(OH)₃, for example, the so-called "concentrated aqua ammonia" is used. It might be advantageous to know the strength of this reagent in terms of iron.

Example 2. Calculate the Fe-titre of concentrated ammonia reagent.

From the specific-gravity table (Appendix) it is noted that the concentrated reagent has a specific gravity of 0.900 and a percentage purity, computed in terms of NH₃, of 28.33 per cent. Each cubic centimeter therefore contains

$$0.900 \times 0.2833 = 0.255 \text{ gram of NH}_3$$

This is the NH₃-titre of the ammonia solution. From the reactions



the proportionality is Fe : 3OH⁻ : 3NH₃, or simply, Fe : 3NH₃. We have then

$$\frac{\text{Fe}}{3\text{NH}_3} = \frac{55.84}{3 \times 17.034} = \frac{x}{0.255}$$

$$x = 0.2788 \text{ gram Fe per cubic centimeter}$$

Or, from the chemical factor, $\frac{55.84}{3 \times 17.034} = 1.095$, we have

$$0.255 \times 1.095 = 0.2788 \text{ gram Fe per cubic centimeter}$$

Volume of Precipitating Reagent Required. It is usually necessary to calculate, in advance, the volume of precipitating agent required in a

gravimetric determination. An excess beyond that required by the stoichiometric proportion is always added to insure as complete a precipitation as possible. In order to calculate the volume required, the approximate amount of constituent in the sample should be known, or, if this information is lacking, it is assumed, for this calculation, that the sample is pure.

Example 3. What volume of AgNO_3 solution containing 20 grams of AgNO_3 per liter will be required to precipitate the chloride, as AgCl , in a 0.2500-gram sample of NaCl ?

Assume the sample to be pure NaCl . Calculate the Cl -titre of the AgNO_3 solution. This has already been done in Example 1 and found to be 0.004174 gram per cubic centimeter. Since the sample weighs 0.2500 gram, the total weight of Cl in the sample is

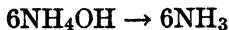
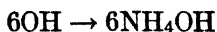
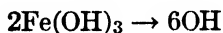
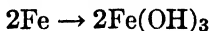
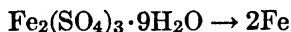
$$0.2500 \times \frac{35.46}{58.46} = 0.1516 \text{ gram Cl}$$

Therefore

$$0.1516 \div 0.004174 = 36.32 \text{ cc.}$$

Example 4. What volume of concentrated ammonium hydroxide (sp. gr. 0.900, containing 28.33 per cent of NH_3 by weight) is required to precipitate as $\text{Fe}(\text{OH})_3$, the Fe contained in 5.0000 grams of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$?

There is a long, round-about way, but also a simple short way, to calculate the weight and hence the volume of the reagent required. Setting up the necessary series of equations and relationships involved, we have



We might thus, ridiculously, set up six separate definite proportions and calculate, in turn, the weight of Fe , $\text{Fe}(\text{OH})_3$, OH , NH_4OH and finally the weight of NH_3 . That this is needless labor is seen at once by the ratios:

$$\frac{2\text{Fe}}{\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}} = \frac{2\text{Fe}(\text{OH})_3}{2\text{Fe}} = \frac{6\text{OH}}{2\text{Fe}(\text{OH})_3} = \frac{6\text{NH}_4\text{OH}}{6\text{OH}} = \frac{6\text{NH}_3}{6\text{NH}_4\text{OH}}$$

in which common members cancel out, leaving the significant ratio

$$\frac{6\text{NH}_3}{\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}}$$

Therefore
$$\frac{6\text{NH}_3}{\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}} = \frac{\text{grams of NH}_3}{\text{wt. of sample}}$$

$$\frac{6 \times 17.034}{562.001} = \frac{x}{5.0000}$$

$$x = 0.9093 \text{ gram NH}_3$$

Then, volume of ammonia \times sp. gr. \times per cent NH_3 = grams of NH_3
or

$$\frac{0.9093}{0.900 \times 0.2833} = 3.57 \text{ cc. of reagent}$$

CALCULATION OF SAMPLE WEIGHTS

An understanding of the proper weight of sample to use in a gravimetric determination is one of the criteria which distinguish the thoughtful experimenter from the casual cook-book worker. The chief factor which determines the amount of sample is the facility with which the precipitate can be washed, purified, filtered, dried or ignited and finally weighed. On the one hand the capacity of the beakers, funnels and crucibles limits the maximum bulk of precipitate whereas, on the other hand, enough precipitate or final product must be obtained so that the errors in weighing are not unduly large. The amount of sample to take, furthermore, depends upon the amount of constituent in the sample. Thus if one sample is thought to contain about 20 per cent of constituent, and another about 80 per cent of the same constituent, about four times as much of the first sample would have to be taken in order to yield the same amount of product.

With respect to the capacity of the apparatus it might be said, in general, that such a quantity of precipitate can conveniently be handled that will, when dried or ignited, yield a pure product weighing in decigrams or centigrams, i.e., in the tenths or hundredths of a gram. With less than this, errors made in weighing would be seriously magnified in the final percentage calculation. Much depends upon the physical nature of the precipitate. It should be remembered, of course, that there is a change in weight when the constituent is precipitated and a further change in weight when, if necessary, the precipitate is converted by ignition into another compound.

Example 5. What weight of sample of pure NaCl should be taken so that, when precipitated with AgNO₃, the dried AgCl should weigh 0.2500 gram?

From the reaction



it is obvious that the factor $\frac{\text{NaCl}}{\text{AgCl}}$ gives the direct relationship

$$\frac{\text{NaCl}}{\text{AgCl}} = \frac{58.454}{143.34} = \frac{x}{0.2500}$$

$$x = 0.1019 \text{ gram of sample}$$

If the sample is thought to be about 60 per cent pure, the weight of sample would be

$$0.1019 \div 0.60 = 0.1699 \text{ gram}$$

Example 6. What weight of sample containing iron, such as FeSO₄ · (NH₄)₂SO₄ · 6H₂O, should be taken for analysis, so that, when the sample is dissolved, the iron oxidized, precipitated as Fe(OH)₃ and ignited to Fe₂O₃, the Fe₂O₃ will weigh about 0.2 gram, assuming the sample to contain 10 per cent iron?

$$\frac{2\text{Fe}}{\text{Fe}_2\text{O}_3} = \frac{x}{0.2}$$

or

$$x = 0.6994 \times 0.2 = 0.1399 \text{ gram Fe}$$

in 0.2 gram of Fe₂O₃. Since the sample is thought to be 10 per cent pure iron, the weight of sample will be

$$0.1398 \div 0.10 = 1.3988 \text{ grams of sample}$$

Problems of this kind can of course be solved by substitution in the formula for percentage calculations, viz.,

$$\frac{\text{Wt. of precipitate} \times \text{Chemical factor}}{\text{Weight of sample}} \times 100 = \text{percentage}$$

$$\frac{0.2 \times 0.6994}{x} \times 100 = 10.0$$

$$x = 1.3988$$

An interesting question arises in connection with the weighing of samples. Is it always necessary to weigh the sample to the usual one-tenth of a milligram? The following consideration with regard to the

foregoing example will throw light on this question. It was found that in order to obtain 0.2000 gram of ignited Fe_2O_3 from a 10 per cent iron sample, a 1.3988-gram sample must be taken. Suppose the sample contains only 1 per cent of iron; then the same weight, 1.3988 grams, will yield only 0.0200 gram of Fe_2O_3 . What would be the effect if only 1.39 grams of sample were taken? The weight of Fe_2O_3 in this case is 0.0199 gram, differing by a negligible 0.1 of a milligram. In this case, it would be unnecessary to weigh beyond the centigram unit, i.e., to the second decimal place. In other cases, where the constituent runs high, it is necessary to weigh the sample to 0.0001 of a gram.

Factor-Weight Samples. A chemical factor, we have already seen, is the ratio of the molecular or atomic weight of the constituent sought to the molecular weight of the compound to which the constituent is equivalent. When applied to gravimetric analysis a chemical factor is the weight, in grams, of constituent contained in or equivalent to 1 gram of the ignited precipitate. In the calculation of gravimetric data, we have the relation:

$$\text{Weight of precipitate} \times \text{Chemical factor} = \text{Weight of constituent}$$

and to calculate the percentage of constituent from the weight of an impure sample and the weight of the precipitate we have:

$$\frac{\text{Weight of precipitate} \times \text{Chemical factor}}{\text{Weight of sample}} \times 100 = \text{Percentage of constituent}$$

A special use of chemical factors follows from this relationship, in that, if the weight of the sample is selected numerically equal to the chemical factor, these two terms cancel and we have directly the weight of the precipitate multiplied by 100 equal to the percentage of constituent. Then each 0.01 of a gram (each centigram) of precipitate will represent 1 per cent of constituent, and each milligram will represent 0.1 of one per cent. A weight of sample in grams equal to the chemical factor is known as a factor-weight sample.

As an example, suppose that it is desired to take such a weight of a sulfate-containing sample, for example impure sodium sulfate, that the weight of the precipitated BaSO_4 should equal the percentage of SO_4 present. Since

$$\frac{\text{Weight of BaSO}_4 \times \frac{\text{SO}_4}{\text{BaSO}_4}}{\text{Weight of sample}} \times 100 = \text{Percentage of SO}_4,$$

and the chemical factor of SO_4 in BaSO_4 is 0.4116, then, if a 0.4116-gram sample is taken, the equation becomes:

$$\frac{\text{Weight of BaSO}_4 \times 0.4116}{0.4116} \times 100 = \text{Percentage of SO}_4$$

From this it is evident that, when the weight of BaSO_4 is multiplied by 100, the product will represent directly the percentage of the desired constituent. If, for example, 0.01 gram of BaSO_4 is obtained, it will represent 1 per cent of SO_4 in the sample.

In general, the relationship holds true:

$$\frac{0.01 \times \text{Chemical factor}}{\text{Factor-weight sample}} \times 100 = 1 \text{ per cent}$$

in which the chemical factor is that required to convert the precipitate to the desired constituent and each 0.01 of a gram of precipitate represents 1 per cent, if the weight of sample taken is the factor weight.

The use of factor-weight samples has the advantage in certain analyses in that no calculations of the results of a determination are necessary. Frequently a tare equal to the factor weight is used, thus avoiding loss of time and errors in placing fractional weights on the pan of the balance. The use applies to samples which are finely powdered and has no advantage where much time is consumed in obtaining an exact factor-weight sample.

PROBLEM SET 12

GRAVIMETRIC REAGENTS AND SAMPLE WEIGHTS

221. What volume of barium-chloride reagent containing 20 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter will be required to precipitate as BaSO_4 the SO_4 contained in 0.2000 gram of pure Na_2SO_4 ? *Ans.* 17.20 cc.

222. How much silver chloride will be precipitated by adding 25 cc. of AgNO_3 (20 grams AgNO_3 per liter) to a sample of impure NaCl ?

223. If a 0.2500-gram sample of chloride (here assumed to be pure NaCl) is dissolved in 50 cc. of water and is to be precipitated as silver chloride with silver-nitrate reagent so that not more than 50 cc. of reagent will be used, how many grams of AgNO_3 per liter should be used in the preparation of the reagent? *Ans.* 14.53 grams.

224. A chemist in dissolving a sample of material used 5 cc. of HCl , sp. gr. 1.12, and then 10 cc. of HNO_3 of sp. gr. 1.42. What volume of concentrated NH_4OH (sp. gr. 0.90, containing 28.33 per cent of NH_3 by weight) should be used to neutralize the solution?

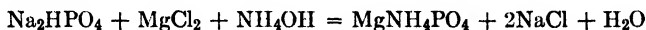
225. What volume of aqua ammonia (concentrated ammonium hydroxide) sp. gr. 0.900, will be required to neutralize 10 cc. of HNO_3 of sp. gr. 1.250? *Ans.* 5.27 cc.

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226. What volume of HCl, sp. gr. 1.120 will be required to react with 0.1872 gram of pure silver? If the sample is an alloy containing 90 per cent silver?

227. What weight of NH_3 will be required to precipitate the iron as $\text{Fe}(\text{OH})_3$ in 0.2500 gram of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$? If the ammonia reagent has a sp. gr. of 0.966, what volume of the reagent will be required? *Ans.* 0.0455.

228. What weight of Na_2HPO_4 would you take for the preparation of a liter of reagent of such a strength that each cubic centimeter will precipitate 0.005 gram of magnesium according to the reaction?



229. If you wished to prepare an ammonium-hydroxide solution for the precipitation of $\text{Al}(\text{OH})_3$, so that each cubic centimeter would bring into reaction 0.003 gram of Al, what volume of "aqua ammonia" (sp. gr. 0.900, containing 28.33 per cent NH_3) would be required for one liter of the basic reagent?

Ans. 21.6 cc.

230. An ammonium-hydroxide solution, 1 cc. of which will precipitate 0.003 gram of Al as $\text{Al}(\text{OH})_3$, will precipitate, per cubic centimeter, how much Fe as $\text{Fe}(\text{OH})_3$?

231. What weight of sample of iron-containing material should be taken for analysis so that, in each case, the weight of ignited Fe_2O_3 should not exceed 0.5 of a gram for samples containing (a) 5 per cent Fe, (b) 40 per cent Fe and (c) 70 per cent Fe? *Ans.* (a) 6.994 grams; (b) 0.8743 gram; (c) 0.4994 gram.

232. What is the least weight of sample you would take for the determination of chloride by precipitation and weighing of AgCl, if the sample was thought to contain about 1 per cent of Cl and the AgCl should weigh at least 0.01 of a gram?

233. If a Na_2SO_4 sample is known to be approximately 80 per cent pure, by what simple number would you multiply the chemical factor Na_2SO_4 in BaSO_4 so that a proper weight of sample should be taken? *Ans.* 0.80.

234. The total carbon in steel is determined by burning the sample in a current of oxygen and absorbing and weighing the CO_2 evolved. What weight of steel sample should be taken so that each centigram of CO_2 represents 1.0 per cent of carbon in the steel?

235. What weight of iron ore should be taken for analysis so that, when the iron is precipitated as $\text{Fe}(\text{OH})_3$ and finally weighed as Fe_2O_3 , each milligram when multiplied by 20 should represent 1 per cent of iron in the sample?

Ans. 1.399 grams.

236. What weight of zinc ore should be taken for analysis so that, when the zinc is precipitated and weighed as ZnNH_4PO_4 , each milligram of the precipitate shall equal 0.1 of 1 per cent of zinc? If the zinc precipitate is ignited to $\text{Zn}_3\text{P}_2\text{O}_7$?

237. Two samples of soluble chlorides of 0.3000 gram each, known to contain, respectively, 10 per cent and 90 per cent of chloride, were submitted for analysis. In the precipitation filtration and weighing of the AgCl precipitates, errors amounting, in each case, to 0.5 of a milligram were introduced. What was the percentage error in each case? *Ans.* (a) 0.41 per cent; (b) 0.046 per cent.

238. A series of NaCl samples were submitted for analysis. A 0.2500-gram sample was taken in each case. The percentages of Cl known to be present were as follows: 5, 10, 25, 50, 75, 90 and 95 per cent respectively. (a) Suppose an error of 0.3 milligram was made in the weighing of each sample; what percentage error was made in each case? (b) If an error of 0.3 milligram is made in the weighing of the AgCl precipitates, what were the percentage of errors made in the analyses?

239. A student made a determination of the SO_4 in a sample of material, obtaining in a triplicate analysis 0.7562, 0.7580 and 0.7586 gram of BaSO_4 . What was the precision of his determination, in parts per thousand? If the precision of a sulfate determination is 3 parts per thousand, should any of the results be rejected?

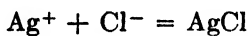
Ans. (a) 1.8; (b) 0.5; (c) 1.3; No.

240. A 0.2000-gram sample of pure NaCl should yield what weight of AgCl? A 0.2000-gram sample of NaCl, 50 per cent pure, should yield what weight of AgCl? If, in each case, the error is not to be greater than 2 parts per thousand, what maximum and minimum weights of AgCl might be obtained?

CHAPTER VIII

EQUILIBRIA IN GRAVIMETRIC PRECIPITATION ANALYSIS

A precipitation reaction takes place because ions unite to form a not readily soluble solid product. An ionic equilibrium is established between the interacting ions, and is rigorously controlled by the solubility product principle. This principle, a fundamental application of the Law of Chemical Equilibrium, concerns itself with the equilibria between ions in solutions in which precipitates are forming. The principle states that the product of the gram-ion concentrations of the ions reacting to form a precipitate is always a constant. Thus, in a simple case, such as the reaction between Ag^+ ions and Cl^- ions



the concentrations, when multiplied together, give, at constant temperature, a numerical constant called the solubility product constant and designated, in this book, by the symbol $K_{s.p.(\text{AgCl})}$

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{s.p.(\text{AgCl})}$$

In cases where three different ions combine, as in the formation of MgNH_4PO_4 , the solubility product equation is

$$C_{\text{Mg}^{++}} \times C_{\text{NH}_4^+} \times C_{\text{PO}_4^{--}} = K_{s.p.(\text{MgNH}_4\text{PO}_4)}$$

And in cases where two or more ions of one kind unite with one or more ions of another kind, as in the precipitation of $\text{Mg}(\text{OH})_2$, the solubility product equation is

$$C_{\text{Mg}^{++}} \times C_{\text{OH}^-} \times C_{\text{OH}^-} = K_{s.p.}$$

or

$$C_{\text{Mg}^{++}} \times (C_{\text{OH}^-})^2 = K_{s.p.(\text{Mg}(\text{OH})_2)}$$

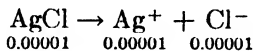
Calculation of Solubility Product Constants. These equilibrium constants are calculated from solubility data. The method of calculation is here shown by the following example.

Example 1. Calculate the $K_{s.p.}$ of AgCl . Experiment shows that 0.0015 gram of pure AgCl will dissolve in a liter of water at room temper-

ature. The gram solubility, divided by the molecular weight of AgCl , will give the molar solubility.

$$\frac{0.0015}{143.34} = 0.00001 \text{ of a gram-mole}$$

That is, 0.00001 of a gram-mole of AgCl will dissolve in a liter of water to form a saturated solution of this salt. This is an extremely dilute solution and may be considered completely ionized. We have therefore



and the concentrations of both silver and chloride are 0.00001 of a gram-ion per liter.

We have therefore

$$\begin{array}{ccc} C_{\text{Ag}^+} \times C_{\text{Cl}^-} & = & K_{s.p.} \\ 0.00001 & & 0.00001 = 1.110 \times 10^{-10} \end{array}$$

Application of the Solubility Product Principle to Precipitation.

In a precipitation reaction, equilibrium is *first* reached when the product of the concentrations of the ions equals the solubility product constant of the precipitate. A slight excess of precipitating reagent beyond this concentration is necessary to cause the initial formation of the precipitate. Let us illustrate by an example.

Example 2. What concentration of Ag^+ ion is necessary to establish equilibrium and hence to initiate the precipitation of AgCl in a liter of solution which has a Cl^- -ion concentration of 0.01 gram-ion?

Since the product of the concentrations of the silver and chloride ions must equal the $K_{s.p.}$ of AgCl , 1.1×10^{-10} , the equation

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{s.p.(\text{AgCl})}$$

can readily be solved, letting x stand for the concentration of the silver ion.

$$x \times 1.0 \times 10^{-2} = 1.1 \times 10^{-10}$$

whence x equals approximately 1.1×10^{-8} . This quantity of Ag^+ ion must be added before the solution is saturated with respect to both Ag^+ ion and Cl^- ion. Visible precipitation will not occur until an excess of Ag^+ ion beyond 1.1×10^{-8} has been added.

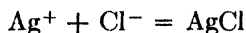
The calculation just made merely tells us under what concentration conditions we can expect a precipitate of AgCl to make its appearance. It serves the purposes of a qualitative test but it does not furnish the data for a (practically) complete quantitative precipitation. In order to find out how complete the precipitation may be made, or, more specif-

ically, how much constituent will remain unprecipitated when final equilibrium is reached, the solubility product principle must be extended.

The concentration of ions which remain in equilibrium when an equivalent amount of precipitating agent has been added can be calculated from the solubility product equation, as illustrated in the following example.

Example 3. What Cl^- -ion and Ag^+ -ion concentrations remain in equilibrium when an equivalent amount of Ag^+ ion has been added to a solution containing Cl^- ions?

If the solution of the sample contained, for example, 0.01 gram-ion of Cl^- per liter, the stoichiometric quantity of Ag^+ for complete reaction would be 0.01 of a gram-ion and there would be produced 0.01 of a gram-mole of AgCl .



$$0.01 + 0.01 = 0.01$$

But this quantity, 0.01 gram-mole of AgCl , does not appear completely as insoluble precipitate, since, according to the solubility data cited in Example 1, AgCl dissolves to the extent of 0.00001 gram-mole per liter. There remain unprecipitated 0.00001 of a gram-mole of AgCl or, in terms of ion concentrations, 0.00001 of 1 gram-ion of chloride ion and a like concentration of silver ion.

The quantity of ion remaining in solution when equivalent amounts of ions have been brought together can be calculated directly from the solubility product equation

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{\text{s.p.}}$$

$$x \times x = 1.1 \times 10^{-10}$$

$$x^2 = \sqrt{1.1 \times 10^{-10}}$$

$$x = 1 \times 10^{-5}$$

This quantity of Cl^- ion remains in solution if the precipitation is conducted in a liter of solution. Note particularly that the ionic concentrations are independent of the total quantity of ion whose practically complete precipitation is desired. No matter how much or how little of the constituent is present in the sample, the same concentration of ion remains unprecipitated and therefore represents a loss and an error inherent in the reaction.

The conditions just outlined are those fulfilled in a volumetric precipitation method (see Chapter IV). For a gravimetric precipitation method it is important to obtain the maximum possible precipita-

tion, and, for this reason an excess of precipitating reagent beyond the equivalent quantity is added. The concentration of ions, in equilibrium, when this further condition has been satisfied can likewise be calculated from the solubility product equation.

Example 4. What concentrations of Cl^- ion and Ag^+ ion remain in equilibrium when an excess of Ag^+ ion has been added during the precipitation of AgCl ?

Let us assume that an excess of ten times over the equivalent quantity of Ag^+ has been added. From the equation

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = 1.1 \times 10^{-10}$$

for an equivalent amount, the concentrations are both 1×10^{-5} (see Example 3). Then we have here

$$C_{\text{Ag}^+} \times C_{\text{Cl}^-} = K_{\text{s.p.}}$$

$$1 \times 10^{-4} \times x = 1.1 \times 10^{-10}$$

whence x , the Cl^- ion remaining, is 1.1×10^{-6} . By the addition of an excess of Ag^+ ion, the concentration of Cl^- ion has been lowered to 1.1×10^{-6} per liter, and the error in the determination has been reduced correspondingly.

Precipitation under Controlled Conditions. In a number of important determinations, it is necessary to control the concentration of certain ions, particularly the hydrogen, hydroxyl and sulfide ion. This is accomplished by common-ion effect, and a solution, adjusted in this manner, is known as a buffered solution. If a salt of a weakly ionized acid or base is added to a solution of the acid or base, the concentration of the H^+ ion or that of the OH^- ion will not only be lowered but will remain constant at the predetermined concentration. The following example will show how a simple buffered solution is prepared.

Example 5. What will be the hydrogen-ion concentration in a liter of $0.1 \text{ M HC}_2\text{H}_3\text{O}_2$ to which 0.1 of a gram-mole of $\text{NaC}_2\text{H}_3\text{O}_2$ has been added?

It will be of interest first to calculate the hydrogen-ion concentration in the pure solution of $\text{HC}_2\text{H}_3\text{O}_2$ before the sodium acetate is added. This may be done in two ways: If the degree of ionization of the acid is known for the specified molarity, the hydrogen-ion concentration may be found by simply multiplying the molarity by the extent of ionization. For a 0.1 M solution of acetic acid the degree of ionization is 1.34 per cent. Therefore

$$C_{\text{H}^+} = 0.1 \text{ M} \times 0.0134 = 0.00134, \text{ or } 1.34 \times 10^{-3} \text{ gram-ion of H}^+\text{-ion}$$

If on the other hand the degree of ionization is unknown, an approximation of the equilibrium formula is employed for the calculation of the C_{H^+} in a weakly ionized acid.

$$\frac{C_{H^+} \times C_{\text{anion}}}{C_{\text{non-ionized acid}}} = K_{(\text{ion})}$$

$$\frac{x \times x}{\text{Molarity}} = K_{(\text{ion})}$$

where x is the concentration of H^+ -ion as well as anion. As an approximation, the concentration of the non-ionized acid may be taken as the molarity of the acid. In the case of a 0.1 M solution of $HC_2H_3O_2$

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{(\text{ion})}$$

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$x = \sqrt{1.8 \times 10^{-6}}$$

$$= 1.34 \times 10^{-3}$$

The unbuffered solution of 0.1 M acetic acid thus has a hydrogen-ion concentration of 1.34×10^{-3} or 0.00134 gram-ion.

If now a soluble acetate, such as $NaC_2H_3O_2$, is added, the acetate-ion concentration is enormously increased with a corresponding large decrease in the hydrogen-ion concentration. Adding 0.1 of a gram-mole of $NaC_2H_3O_2$ (here assumed completely ionized) will cause a certain amount of H^+ to react with $C_2H_3O_2^-$ to form $HC_2H_3O_2$, and if we let x represent the concentrations of H^+ and $C_2H_3O_2^-$ which combine to form x gram-moles of $HC_2H_3O_2$ the ionic equilibrium, precisely formulated from the equilibrium equation

$$\frac{C_{H^+} \times C_{C_2H_3O_2^-}}{C_{HC_2H_3O_2}} = K_{(\text{ion})}$$

becomes, for a 0.1 M solution of $HC_2H_3O_2$ containing 0.1 of a gram-mole of $NaC_2H_3O_2$

$$\frac{[0.00134 - x] \times [(0.00134 + 0.1) - x]}{[(0.1 - 0.00134) + x]} = 1.8 \times 10^{-5}$$

To solve for x , the amount by which the hydrogen-ion concentration is decreased, involves a quadratic equation. To obviate this, an approxi-

mation may be employed, based on the following considerations: (1) The total acetate concentration is not materially decreased by the small value of x ; (2) the concentration of the non-ionized acid may be taken simply as the molarity of the original solution. We have, letting y equal $0.00134 - x$, i.e., the final resulting hydrogen-ion concentration

$$\frac{y \times 0.1}{0.1} = 1.8 \times 10^{-5}$$

$$y = 1.8 \times 10^{-5}$$

$$= 0.000018$$

The hydrogen-ion concentration has thus been decreased to approximately 0.000018 gram-ion, about a hundredfold.

Example 6. Another example of the same kind may be helpful, in illustrating this approximate method of calculation of hydrogen-ion concentrations. Suppose that, to 1 liter of a 0.5 M solution of $\text{HC}_2\text{H}_3\text{O}_2$, ionized 0.7 per cent, we add 0.3 of a gram-mole of $\text{NaC}_2\text{H}_3\text{O}_2$ which in a liter of solution is ionized about 78 per cent. What is the new hydrogen-ion concentration? The total $\text{C}_2\text{H}_3\text{O}_2$ -ion concentration before equilibrium is established is equal to the sum of 0.3×0.78 , or 0.234, and 0.5×0.007 , or 0.0035. The latter quantity may be neglected, and we may also neglect the amount of acetate which unites with hydrogen ions to form $\text{HC}_2\text{H}_3\text{O}_2$. The concentration of non-ionized $\text{HC}_2\text{H}_3\text{O}_2$ at the start is 0.5×0.993 , or 0.4965 gram-mole, for which we may assume 0.5 M . Then, letting y equal the resulting H-ion concentration, we have:

$$\frac{y \times 0.234}{0.5} = 0.000018$$

from which y equals 0.0000389.

PROBLEM SET 13

EQUILIBRIUM AND BUFFER CALCULATIONS IN GRAVIMETRIC PRECIPITATIONS

241. Calculate the solubility product constants for the following relatively insoluble precipitates, the molar solubility being given.

	Molar Solubility	
(a) CaCO_3	1.3×10^{-4}	<i>Ans.</i> 1.7×10^{-8} .
(b) K_2PtCl_6	2.3×10^{-2}	4.9×10^{-5} .
(c) Ag_2CrO_4	7.5×10^{-5}	1.7×10^{-12} .
(d) PbCrO_4	1.3×10^{-7}	1.7×10^{-14} .
(e) AgBr	5.9×10^{-7}	3.5×10^{-13} .

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242. Calculate the solubility product constants for the following insoluble compounds, the solubility in grams per liter being given:

	Solubilities
(a) AgCNS	1.4×10^{-4}
(b) Mg(OH) ₂	1.2×10^{-2}
(c) MgNH ₄ PO ₄	8.6×10^{-3}
(d) Fe(OH) ₃	4.8×10^{-8}
(e) Cu ₂ I ₂	2.1×10^{-6}

243. For the following weights of sample assumed to be the pure salt, calculate the grams of precipitating ion required to start the precipitation of the corresponding compounds for which the solubility product constants are given. In each case the total volume of solution is 200 cc.

	$K_{s.p.}$		Ans.
(a) 0.2500 NaCl	AgCl	$= 1.1 \times 10^{-10}$	5.6×10^{-7} .
(b) 0.7500 Na ₂ SO ₄	BaSO ₄	$= 1.2 \times 10^{-10}$	6.3×10^{-7} .
(c) 1.0000 Fe(SO ₄) ₂ (NH ₄) ₂ SO ₄ ·6H ₂ O	Fe(OH) ₃	$= 1.1 \times 10^{-36}$	7.5×10^{-9} .
(d) 0.5005 CaCO ₃	CaC ₂ O ₄	$= 3.9 \times 10^{-9}$	7×10^{-5} .
(e) 0.7500 MgSO ₄	MgNH ₄ PO ₄	$= 2.5 \times 10^{-13}$	2.66×10^{-4} .

244. Calculate the gram-ion concentrations of the precipitating ions required to establish equilibrium and therefore to start precipitation of the respective products, the concentration of the ions to be precipitated being in each case 0.01 gram-ion.

	$K_{s.p.}$	
(a) Cl ⁻	AgCl	$= 1.1 \times 10^{-10}$
(b) Mg ⁺⁺	Mg(OH) ₂	$= 3.5 \times 10^{-11}$
(c) PO ₄ ⁼	MgNH ₄ PO ₄	$= 2.5 \times 10^{-13}$
(d) Mn ⁺⁺	MnS	$= 1.4 \times 10^{-15}$
(e) Pb ⁺⁺	PbCrO ₄	$= 1.7 \times 10^{-14}$

245. When the equivalent amount of precipitating agent has been added corresponding to the balanced equation what are the gram-ion concentrations remaining in solution for the following cases, the solubility product constants of which are given.

(a) AgCl, $K_{s.p.} = 1.1 \times 10^{-10}$	Ans. 1.05×10^{-5} .
(b) AgBr, $K_{s.p.} = 3.5 \times 10^{-13}$	5.9×10^{-7} .
(c) AgI, $K_{s.p.} = 1.7 \times 10^{-16}$	1.3×10^{-8} .

246. If in the precipitation of Fe(OH)₃ the addition of NH₄OH were halted when the equivalent amount of hydroxyl had been added, what weight in grams of Fe⁺⁺⁺ ion would remain unprecipitated, the final volume of solution being 400 cc.? The $K_{s.p.}$ of Fe(OH)₃ is 1.1×10^{-36} .

✓ **247.** What is the percentage error introduced in the determination of a 0.2000-gram sample of pure oxalic acid, if the precipitation with a solution of CaCl₂ is stopped when an equivalent quantity is added? $K_{s.p.}$ of CaC₂O₄ is 3.8×10^{-9} , and total volume is 250 cc. Ans. 0.7 per cent.

248. If, in a series of precipitations of silver, as AgCl, by means of HCl, the precipitations are stopped at the equivalent point, and the volumes of solution are

respectively 100 cc., 200 cc., 500 cc., 750 cc. and 1000 cc., what amounts of silver (gram quantities) remain in solution? The $K_{s.p.}$ of AgCl is approximately 1.1×10^{-10} .

249. If in the precipitation of silver chloride from a 0.2500-gram sample of pure NaCl an excess of 10 per cent over the amount demanded by the stoichiometric quantity is added, what are the Ag^+ and Cl^- concentrations remaining, assuming a liter of final solution?

$$\text{Ans. } C_{\text{Ag}^+} = 4.3 \times 10^{-4}.$$

$$C_{\text{Cl}^-} = 2.6 \times 10^{-7}.$$

250. Calculate the hydrogen-ion concentration of solutions of the following concentration: (a) 0.1 M (normal) HCl 92.0 per cent ionized, (b) 0.1 M (normal) NaOH 90.5 per cent ionized, (c) 150 cc. of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$, 1.34 per cent ionized.

251. From the data given calculate the equilibrium ratios (ionization constants) for the following weakly ionized electrolytes:

Ans.

(a) 0.01 M (normal) $\text{HC}_2\text{H}_3\text{O}_2$, 4.17 per cent ionized	1.82×10^{-5} .
(b) 0.1 M (normal) HCN 0.01 per cent ionized	1×10^{-9} .
(c) 0.01 M (normal) NH_4OH 4.07 per cent ionized	1.74×10^{-5} .
(d) 0.1 M (normal) HCHO 4.5 per cent ionized	2×10^{-4} .

252. From the ionization constants given calculate the hydrogen-ion concentration for each of the following solutions:

(a) 0.01 M $\text{HC}_2\text{H}_3\text{O}_2$ $K_{(\text{ion})}$	1.8×10^{-5}
(b) 0.1 M NH_4OH $K_{(\text{ion})}$	1.75×10^{-5}
(c) 0.1 M H_2S $K_{(\text{ion})}$	1.1×10^{-23}

253. Calculate, from ionization data, the hydrogen-ion concentrations of 0.1 M solutions of HCl and $\text{HC}_2\text{H}_3\text{O}_2$. (b) Which has the greater acidity? (c) Which one, if either, will neutralize the greater volume of 0.1 M NaOH ?

$$\text{Ans. } 0.092. \quad 0.00134.$$

(b) HCl .

(c) Both the same.

254. What is the concentration of OH^- ions in a liter of solution, 0.1 M with respect to NH_4OH and 0.5 M with respect to NH_4Cl ? $K_{(\text{ion})}$ of NH_4OH is 1.75×10^{-5} ; degree of ionization of NH_4Cl is 78.2 per cent.

255. To what extent would you have to dilute a molar solution of $\text{HC}_2\text{H}_3\text{O}_2$, so that the C_{H^+} had a value of approximately 10^{-5} ? How much dilution would be required of a molar solution of HCl to reach the same value? (See Ionization Tables for data.)

$$\text{Ans. } (a) 5.6 \times 10^{-6}.$$

$$(b) 1 \times 10^{-5}.$$

256. In order to maintain a C_{H^+} of 10^{-4} by use of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$, how many grams of $\text{NaC}_2\text{H}_3\text{O}_2$ must be added to 200 cc. of the solution which is 0.05 M with respect to acetic acid? The ionization constant for acetic acid is 1.8×10^{-5} ; assume the ionization of the added salt to be 80 per cent.

257. If you wished to precipitate a sulfide, MS , whose $K_{s.p.}$ is 1×10^{-30} and the metal-ion concentration was 1×10^{-3} , what sulfide-ion concentration would have

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to be maintained? Would the sulfide precipitate if the solution contained enough HCl to make the total acidity, as indicated by the C_{H^+} , 10^{-2} ?

Ans. (a) 1×10^{-27} ; (b) yes.

258. What will be the hydrogen-ion and sulfide-ion concentrations in a liter of solution which contains 25 cc. of HCl (sp. gr. 1.19 and 37 per cent pure HCl) and into which H_2S is passed? $(C_{H^+})^2 \times C_{S^{2-}} = 1.1 \times 10^{-23}$.

259. If we buffer a H_2S solution by means of HCl, so that the total hydrogen-ion concentration is respectively (a) 10^{-4} , (b) 10^{-3} , (c) 10^{-2} and (d) 10^{-1} , what is the resulting sulfide-ion concentration. The equilibrium equation is $(C_{H^+})^2 \times C_{S^{2-}} = 1.1 \times 10^{-23}$.

Ans. (a) 1.1×10^{-15} .

(b) 1.1×10^{-17} .

(c) 1.1×10^{-19} .

(d) 1.1×10^{-21} .

260. If in a quantitative separation by precipitation of a sulfide by hydrogen sulfide it is desired to prevent the precipitation of FeS , what can the maximum concentration of sulfide ion be if the amount of Fe^{++} corresponds to 0.001 gram-ion per liter ($K_{s.p.}$ of $FeS = 3.7 \times 10^{-19}$); $(C_{H^+})^2 \times C_{S^{2-}} = 1.1 \times 10^{-23}$. In order to establish this sulfide-ion concentration what must be the hydrogen-ion concentration?

PART IV

CALCULATIONS BASED ON ANALYTICAL DATA

CHAPTER IX

SYSTEMATIC QUANTITATIVE ANALYSIS

A complete quantitative analysis calls for the determination of each constituent present in a given material. If the constituents are to be determined and reported as amounts or percentages of the several elements present in a compound or mixture of compounds, the analysis is called an *ultimate analysis*. The term is sometimes extended to include simple groups or radicals such as the sulfate, phosphate, oxalate or ammonium ions. On the other hand, the needs of a chemical analysis may be served better by what is known as a *proximate analysis*. In a proximate analysis, instead of determining elements or simple groups as such, the analysis is conducted with respect to more complex groups of constituents in the sample. The following illustration may make this distinction clearer.

In a complete ultimate analysis of such a complex material as coal, the total amount of carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus and even silicon, iron, aluminum, etc., would be required, the determination of these elements requiring much skill, time and labor.

A proximate analysis of coal, however, by which moisture, volatile combustible matter, fixed carbon, coke and ash are determined, furnishes much better analytical data in regard to the utilization of this important fuel than would an ultimate analysis.

With either an ultimate or a proximate analysis, if the analysis is complete and perfectly executed, the results, expressed as percentages, must total 100 per cent; all matter composing the sample is thereby accounted for. But it is not always necessary to make complete analyses; frequently the determination of one or two constituents satisfies the purpose for which the analysis is undertaken. Thus, the purity of a substance with respect to a particular constituent may be the sole objective of the analysis, or, conversely, the amount of a certain impurity may be the chief matter of interest in the sample. For example, we

may wish to know the purity of common table salt with respect to NaCl. To do this we would conduct a gravimetric or volumetric determination for chloride, convert this to NaCl on the assumption that all the chloride in the sample is combined with sodium and then, from the weight of sample, compute the percentage purity in terms of NaCl.

Of far greater technical importance is the determination of impurities and such analyses are conducted in the applied chemical industries on a vast scale. In the ferrous metallurgical field, for example, the removal of the harmful impurities in steel, chiefly sulfur and phosphorus, is under rigid analytical control, whereas the iron which constitutes about 98 per cent of the iron-carbon alloy (steel) is omitted from the analysis.

If such partial analyses, either for the determination of the predominating constituents or for those present in minor amounts or as impurities or traces, are to be made, the methods employed must not be interfered with by the presence of other constituents in the sample. The methods may be volumetric, gravimetric or other types of techniques that best suit the particular kind of sample. Likewise, in a complete analysis for all constituents, the methods selected for the determination of the several constituents may be based on any one of the various techniques, depending upon expediency and the nature and probable amount of each constituent. Here an extremely important point cannot be overlooked or overemphasized: The constituents to be determined must, in general, be quantitatively separated one from another, before the final determinations are carried out.

Systematic Quantitative Separations. A quantitative analysis, in its entirety, really involves two sets of analytical operations, namely (1) separations by which each constituent is, in general, completely isolated from all interfering constituents and (2) final determinations, in which, by use of suitable reactions and techniques, the percentage of each is arrived at. In the field of inorganic analysis for the separation of the metals (cations) a systematic scheme of separation has been developed applicable to such materials as rocks, ores, ceramic products, alloys, etc. In fact, this general procedure is the same familiar cation scheme, with certain minor exceptions, used by the student of qualitative analysis, but carried out with greater care and quantitative exactness. Attention has been called to this general procedure by Lundell and Hoffman, of the United States Bureau of Standards in their recent book, *Outlines of Methods of Chemical Analysis*, to which the reader is referred for more details. Suffice it to say here that the major task of chemical analysis is in the separations and not in the final determinations.

For the purpose of qualitative detection, systematic procedures for the separation of the anions are being developed, but as yet no attempt

has been made to apply these schemes to quantitative separations. Consequently, the present methods for the final determination of the anions are selected so that no interference will result.

The data secured as a consequence of making the necessary separations and final determinations constitute the basis from which to compute the percentage composition of the material undergoing complete or partial analysis. The calculations are, in general, of the types already considered. Certain problems in the following problem set illustrate the use of data secured in a systematic series of separations and determinations.

Indirect Analysis. It sometimes happens that, with certain mixtures, a complete separation is not possible or expedient, and as a result two constituents are precipitated together or otherwise determined collectively and not individually. It is usually possible to manage the analysis, in such cases, so that one of the constituents can be indirectly determined, or other data secured by which the amounts of both can be calculated.

In certain instances, such as the determination of the alkali metals, sodium and potassium, the difficulty is overcome in the following way. In the systematic removal of all other cations following the procedure of the general scheme of separation the final filtrate will contain these two elements. By fuming down with H_2SO_4 and evaporating the solution to dryness, a residue of Na_2SO_4 and K_2SO_4 remains. This residue is weighed. The residue may then be dissolved and the potassium precipitated as K_2PtCl_6 or KClO_4 . From this the weight of potassium can be found which, when recalculated as K_2SO_4 and subtracted from the total weight of residue, gives, by difference, the weight of Na_2SO_4 and hence the weight of sodium.

Example 1. In analyzing a mixture of iron and aluminum experimentally the difficulty can be overcome by first precipitating the mixture with NH_4OH , igniting the mixed $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ to Al_2O_3 and Fe_2O_3 and weighing the mixture of oxides. The mixture of oxides may then be dissolved or another sample taken and, by a separate (volumetric) analysis, the amount of iron can be determined. Then, by calculating the weight of Fe_2O_3 equivalent to the amount of iron found, and subtracting this from the total weight of mixed oxides, the weight of Al_2O_3 can be found.

Instead of determining one of the constituents by a separate procedure, and calculating the other by difference, as illustrated in the foregoing examples, it is possible with certain mixtures which have a common constituent to make a separate determination of this common

constituent. The calculations are then more complicated. A sample calculation is made in the following problem.

Example 2. A sample of material contained, among other constituents, a chloride and a bromide. A weighed portion was dissolved and treated with an excess of AgNO_3 , precipitating a mixture of AgCl and AgBr weighing 0.8413 gram. By a separate analysis of this mixture the total amount of silver was found to be 0.5678 gram. What are the weights of chlorine and bromine in the sample?

We know the total weight of the mixture of AgCl and AgBr and the total weight of silver which is partly combined with the chlorine and partly with the bromine. In order to find the amounts of chlorine and bromine, we must first calculate the separate weights of AgCl and of AgBr . Letting x stand for the weight of AgCl and y for the weight of AgBr , we have the equation:

$$x + y = 0.8413 \text{ gram} \quad (1)$$

The weight of silver combined as AgCl is found from the relation:

$$\text{Ag} : \text{AgCl} = \text{weight of Ag in AgCl} : x$$

or

$$\frac{\text{Ag}}{\text{AgCl}} x = \text{weight of Ag in AgCl}$$

and the weight of silver combined as AgBr is:

$$\text{Ag} : \text{AgBr} = \text{weight of Ag in AgBr} : y$$

or

$$\frac{\text{Ag}}{\text{AgBr}} y = \text{weight of Ag in AgBr}.$$

The total weight of silver, which has been found by experiment to be 0.5678 gram, is therefore related to the weights of AgCl and AgBr by the equation:

$$\frac{\text{Ag}}{\text{AgCl}} x + \frac{\text{Ag}}{\text{AgBr}} y = 0.5678 \text{ gram} \quad (2)$$

Inserting the proper atomic and molecular weights, equation (2) becomes:

$$\frac{107.88}{143.34} x + \frac{107.88}{187.80} y = 0.5678$$

Using the above ratios as chemical factors of Ag in AgCl and of Ag in AgBr we have the two equations:

$$0.7526x + 0.5744y = 0.5678$$

$$x + y = 0.8413$$

Solving these simultaneous equations, by the elimination of y we have:

$$\begin{array}{rcl} 0.7526x + 0.5744y & = & 0.5678 \\ 0.5744x + 0.5744y & = & 0.4832 \\ \hline 0.1782x & & = 0.0846 \\ x & & = 0.4747 \end{array}$$

Therefore x , the weight of AgCl , is equal to 0.4747 gram. The value for y may now be found from equation (1):

$$\begin{aligned} x + y &= 0.8413 \\ y &= 0.8413 - 0.4747 \\ y &= 0.3666 \end{aligned}$$

Therefore y , the weight of AgBr , is equal to 0.3666 gram. Finally the amount of chlorine is $\frac{\text{Cl}}{\text{AgCl}} \times 0.4747 = 0.1174$ gram, and the amount of bromine is $\frac{\text{Br}}{\text{AgBr}} \times 0.3666 = 0.1560$ gram.

In general, data which involve a common constituent such as a mixture of silver salts, mixed sulfates of the alkalis or alkaline earths, mixed carbonates, etc., must be resolved into two equations, one of which usually embodies the chemical factors, and these equations must then be solved simultaneously.

Recalculation of Percentages to a Changed Basis. It sometimes becomes necessary to convert the results of an analysis to a basis other than that upon which the analyses were made. This is particularly true where the moisture content of the material has an important bearing on the composition as a whole. Samples of material contain more or less moisture particularly if the samples were obtained from raw materials which are hygroscopic or have been exposed to moist surroundings. Ores, limestones, cements, clays, coals and similar substances are of this character. Such samples are sometimes air dried or, more frequently, the analysis is made on moisture-free portions, and a moisture determination is made at the same time.

Analyses are corrected to a moisture-free basis if the determinations have been made on undried samples; if, on the other hand, the analysis was conducted on dried samples, the percentages may be recalculated from the moisture-free basis to an "as-received" basis. It is important to understand the method of calculation in either case.

Example 3. Suppose samples of coal were found to contain 10 per cent of moisture and 40 per cent of volatile combustible matter, the

latter determination being made (a) on an undried sample, (b) on a dried sample. What is the percentage of the latter constituent in either case?

In the first case, since the dry material comprised 90 per cent of the as-received sample and 40 per cent of this is volatile combustible content, then its percentage on a dry basis is $\frac{100}{90}$ of 40 per cent, or 44.4 per cent.

In the second case, a sample of coal which originally contained 10 per cent moisture, and gave, on analysis of the moisture-free sample, a volatile combustible content of 40 per cent, would contain on the as-received basis 40 per cent of 90 per cent, or 36 per cent.

PROBLEM SET 14

SYSTEMATIC ANALYSIS; INDIRECT ANALYSIS; CALCULATION OF PERCENTAGE TO CHANGED BASIS

261. If a chemist analyzes a mixture of equal parts by weight of pure CaCO_3 and MgCO_3 , what percentages of CaO , MgO and CO_2 will he find?

Ans. 28.02 per cent of CaO .
23.91 per cent of MgO .
48.07 per cent of CO_2 .

262. What is the percentage of CaO , MgO and CO_2 in a sample made up by mixing equal gram-molecular parts of pure CaCO_3 and MgCO_3 ?

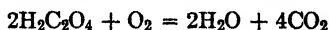
263. A 0.3000-gram sample of brass, containing tin, lead, copper and zinc was subjected to a complete systematic analysis. After proper treatment in the procedure there were obtained: 0.0085 gram of SnO_2 ; 0.0034 gram of PbSO_4 ; after dilution of the filtrate from the lead determination to 250 cc., the electrolysis of a 50-cc. portion of this diluted solution gave 0.0452 gram of Cu ; and 0.03416 gram of $\text{Zn}_2\text{P}_2\text{O}_7$ from the 50-cc. portion. Calculate the percentages of Sn , Pb , Cu and Zn in the sample.

Ans. 2.22 per cent Sn .
0.78 per cent Pb .
75.28 per cent Cu .
24.42 per cent Zn .

264. A partial analysis of a sample of limestone gave the data, when reported as oxides, as shown below. Recalculate the composition of the sample in terms of the metallic elements present.

Reported	Percentage
SiO_2	18.00
Al_2O_3	5.70
Fe_2O_3	1.50
CaO	37.65
MgO	2.00

265. If a 1-gram sample of pure $\text{H}_2\text{C}_2\text{O}_4$ is placed in an organic combustion furnace and burned in a stream of oxygen, according to the reaction



what weight of H_2O and CO_2 should be collected in the absorption units?

Ans. 0.2002 gram of H_2O .
0.9776 gram of CO_2 .

266. In an organic combustion analysis, oxygen was passed over an organic compound containing C, H, O. The sample weighed 0.8652 gram. The gain in weight of the CaCl_2 tube was 0.0869 gram and that of the KOH tube 0.7943 gram. Calculate the percentages of C, H and O in the sample.

267. In the systematic analysis of limestone, the iron and aluminum were precipitated as hydroxides, converted to a mixture of Fe_2O_3 and Al_2O_3 and weighed. The weight of mixed oxide was 0.2934 gram from a 1.5-gram sample. A separate dichromate titration for iron gave 5.62 per cent in the limestone. Calculate the percentage of aluminum.

Ans. 6.10 per cent.

268. A sample of limestone was shown to contain 40.00 per cent of CaO . The CO_2 in the sample evolved from both MgCO_3 and CaCO_3 was 38.50 per cent. What was the percentage of MgCO_3 in the sample?

269. An 0.8000-gram sample of feldspar produced after removal of other constituents a residue consisting of a mixture of K_2SO_4 and Na_2SO_4 weighing 0.2476 gram. After dissolving this residue and converting the K_2SO_4 into K_2PtCl_6 a 0.2954 gram precipitate of the latter compound was obtained. Calculate the percentages of K_2O and Na_2O corresponding to the K and Na present in the rock.

Ans. 7.12 per cent K_2O .
7.72 per cent Na_2O .

270. A mixture of AgCl and AgBr weighing 1 gram was treated with chlorine in order to convert the AgBr into AgCl . After such treatment the mixture weighed 0.9500 gram. Calculate the percentages of Cl and Br in the original mixture.

271. A 1-gram sample of feldspar rock yielded a mixture of KCl and NaCl weighing 0.2178 gram. This mixture of chlorides was dissolved, treated with an excess of AgNO_3 and the AgCl obtained was filtered and weighed. It weighed 0.4775 gram. Calculate the percentages of K and Na in the sample.

Ans. 4.38 per cent Na.
5.58 per cent K.

272. A mixture of AgCl and AgBr was found to weigh 1.0000 gram. The silver in this mixture weighed 0.7500 gram. What are the weights of AgCl and AgBr in the mixture?

273. In the analysis of a certain material after quantitative separation of other constituents, the residue of K_2SO_4 and Na_2SO_4 weighing 0.5231 gram was obtained. This was dissolved and treated with an excess of BaCl_2 giving a precipitate of BaSO_4 which weighed 0.9224 gram. What were the weights of K_2SO_4 and Na_2SO_4 in the residue?

Ans. 0.2904 gram Na_2SO_4 .
0.3327 gram K_2SO_4 .

274. A sample of limestone is shown on analysis to contain 95.00 per cent of a mixture of CaCO_3 and MgCO_3 . The CO_2 in the sample is 46.24 per cent. What are the percentages of MgCO_3 and CaCO_3 ?

275. An iron ore, when received, was found to contain 4.72 per cent of moisture and 46.50 per cent of iron. Calculate the percentage of iron to the dry basis.

Ans. 48.81 per cent Fe.

276. A 5-gram sample of iron ore was dried at 105° C. and lost 0.2250 gram of moisture. A portion of the dried sample was analyzed for iron and found to contain 52.75 per cent of iron. What was the percentage of iron in the sample as "received"?

277. A sample of coal on air drying lost 2.7 per cent in weight. This air-dried sample gave the following results for the proximate analysis: moisture = 1.10 per cent; ash, 5.75 per cent; volatile combustible matter, 35.20 per cent; and fixed carbon, 57.95 per cent. Recalculate the analysis to the (a) as-received, (b) dry or moisture-free and (c) moisture- and ash-free bases.

	(a)	(b)	(c)
<i>Ans.</i> Moisture =	3.77		
Ash =	5.59	5.81	
V.C.M =	34.26	35.59	37.79
F.C. =	56.39	58.59	62.21

278. A cargo of iron ore which at the mine contained 3.0 per cent moisture and 62.00 per cent Fe_2O_3 on a wet basis was shipped to the blast furnace where analysis showed it to contain 6.8 per cent moisture. What percentages of Fe_2O_3 should the blast furnace chemist find (a) on the wet basis, (b) on the dry basis?

279. A sample of Na_2SO_4 , weighing 0.6350 gram and containing 2.50 per cent of moisture, yielded, on the precipitation of the SO_4 , 0.7882 gram of BaSO_4 . Calculate the percentage of SO_3 on the moisture-free basis.

Ans. 43.66 per cent.

280. A sample of coal showed an air drying loss of 5.60 per cent. In making a proximate analysis of portions of the air-dried sample the following values were obtained. Moisture (on air-dried sample) 1.75 per cent; volatile combustible matter 22.65 per cent; fixed carbon 67.20 per cent; ash 8.50 per cent. Calculate these values to (a) the as-received basis, and (b) the moisture-free basis.

CHAPTER X

COMPUTATIONS BASED ON PERCENTAGE COMPOSITION: CALCULATION OF ATOMIC WEIGHTS AND FORMULAS

CALCULATION OF ATOMIC WEIGHTS

The entire structure of chemistry as an exact science rests upon the precision with which the atomic weights of the elements are known. The analytical procedures by which the atomic weights are arrived at are unquestionably the most precise of all quantitative determinations. In general, the method consists in making an exact quantitative determination of the constituent in a carefully purified sample of a compound containing the element the atomic weight of which is to be determined. Such a quantitative determination may not, however, give the true atomic weight but rather a multiple or sub-multiple of it. What is really obtained is the combining weight and not necessarily the atomic weight.

The combining weight is the proportion in which one element will combine with another; the atomic weight is the weight of an atom relative to that of oxygen taken as 16.0000. To illustrate, if we analyze water we find that for every 1.008 grams of hydrogen there are 8.000 grams of oxygen: the combining weight of oxygen is therefore 8.000. If we determine the amount of copper and oxygen in black copper oxide, we find that the copper and oxygen are united in the ratio of 31.78 : 8; whereas in the red oxide of copper the combining proportions of copper to oxygen as determined by experiment are 63.57 : 8. Here we have two different combining weights for copper; and, to arrive at the atomic weight of copper, we must decide which of these combining weights is the atomic weight. With the atomic weight of oxygen fixed at 16.0000, the atomic weight of copper is either 63.57 or 127.14.

To decide whether the combining weight of an element is its atomic weight, or what multiple or sub-multiple of the combining weight to use, involves consideration of other criteria and the application of certain rules and laws. Among these are: (1) The Law of DuLong and Petit, which states that the specific heat of a solid element multiplied by its atomic weight is, in most cases, a constant having the value 6.4. (2) Avogadro's Hypothesis, that equal volumes of gases (under the same con-

ditions of pressure and temperature) contain the same number of molecules. (3) The Periodic Law, in which the element is placed in its proper family relationship. (4) Most of the elements, in the gaseous state, are diatomic. (5) The least common multiple of several combining weights for the same element will, in many cases, indicate the atomic weight.

Applying the last rule to the case of copper previously referred to, where the combining weights are 63.57 and 127.14 respectively, this would indicate the atomic weight of copper to be 63.57. This can be checked by the rule of specific heats, for, if we multiply the specific heat of copper, 0.095, by the atomic weight, we get approximately 6, in sufficient agreement with the constant 6.4 to show that the selected combining weight is the true atomic weight.

During the first half of the nineteenth century, after Dalton's Atomic Theory had been advanced and the combining weights of elements had been worked out with fair accuracy, especially by Berzelius, chemists were not in agreement as to the true atomic weights. It was not until about 1860, when Avogadro's Hypothesis and the valence theory were accepted, that common agreement was reached regarding the atomic weights. Since that time, except for newly discovered elements, atomic weight determinations have consisted in elaboration of the care and precautions in carrying out the analytical procedures, and the modern work annually reported on by the International Committee on Atomic Weights consists chiefly in refinement of technique and revision of the previously reported values.

Example 1. Suppose the atomic weight of sodium is desired. Experimentally, a sample of pure NaCl can be converted to AgCl and thus carefully weighed. If the atomic weights of Cl = 35.457 and Ag = 107.880 are assumed, the atomic weight of Na can be readily calculated from the analytical data.

If 1.0000 gram of pure NaCl yielded 2.4527 grams of AgCl, what is the atomic weight of sodium? By direct proportion:

Weight of NaCl : Weight of AgCl = Mol. wt. of NaCl : Mol. wt. of AgCl

Letting x equal the atomic weight of Na, we have

$$1.0000 : 2.4527 = (x + 35.457) : 143.337$$

from which

$$x = 22.983$$

DERIVATION OF FORMULAS

An important application of quantitative analysis is the use of the data in determining the empirical formulas of pure compounds and minerals. The analysis of a pure chemical compound will show the weight of each element in the weight of sample taken and, by simple calculation, the percentage of each element as well. If the actual weight or the percentage of each element is divided by the atomic weight of that element, the quotient will be the number of gram-atoms of each element present. These gram-atomic weights bear a simple relation to one another such that there will be a common divisor and, if each gram-atomic weight is divided by this common divisor, the ratio of the number of atoms present can be found.

Example 2. Suppose that a 1.0000-gram sample of a pure salt is analyzed and found to be composed of 0.3934 gram of sodium and 0.6065 gram of chlorine. Dividing 0.3934 by the atomic weight of sodium, 22.997, gives 0.01711 gram-atom of sodium; and 0.6065 divided by 35.457 gives 0.01711 gram-atom of chlorine. There are just as many gram-atoms of sodium as there are of chlorine and, consequently, just as many atoms of the one element as of the other. The ratio is 1 : 1, and the simplest formula is NaCl.

The percentages obtained from analysis might just as well be used as the actual weights, the method of calculation being identical in the two cases.

The formula thus obtained is merely the empirical formula, that is, the ratio of the elements composing the compound. The actual molecular formula may be a simple multiple of the empirical formula. A molecular weight determination must be made in order to assign the proper formula to the compound. Various physical-chemical methods are available for determining molecular weights.

PROBLEM SET 15

CALCULATION OF ATOMIC WEIGHTS AND FORMULAS

281. If 5.2685 grams of pure silver yielded, when converted to the bromide, 9.1720 gram of pure AgBr, what is the atomic weight of bromine? Given the atomic weight of Ag = 107.880. *Ans.* 79.93.

282. A 1.0000-gram sample of carefully purified CuO was placed in a heated tube and a stream of hydrogen passed through, by which the oxide was reduced to metallic copper. The weight of copper remaining after the experiment was 0.7990 gram. Calculate the atomic weight of copper.

283. A sample of pure BaSO_4 was found to contain 58.848 per cent of barium. Taking $\text{Ba} = 137.36$ and $\text{O} = 16.000$, calculate the atomic weight of sulfur.

Ans. 32.066.

284. A sample of carefully purified Ag_3PO_4 was found to contain 77.30 per cent of silver. If the atomic weight of Ag is 107.880 and that of oxygen is 16.000, what is the atomic weight of phosphorus?

285. In converting 10.6285 grams of AgBr to AgI , there was found to be an increase of 2.6785 grams. Calculate the atomic weight of iodine, assuming the atomic weights of Ag and Br to be 107.880 and 79.916 respectively.

Ans. 126.93.

286. The atomic weight of manganese was first determined in 1828 by oxidizing 0.5075 gram of the metal to 0.7225 gram of Mn_2O_3 . What value was obtained? More recently, in 1906, the value was redetermined by converting 6.53738 grams of MnBr_2 into 11.43300 grams of AgBr . What was the new value?

287. A 1.0000-gram sample of a certain metal yielded 1.7092 grams of the metallic chloride. If the metal is monovalent, what is its atomic weight? If it is divalent, what is its atomic weight? $\text{Cl} = 35.46$.

Ans. 50; 100.

288. A certain metallic oxide, when converted into the sulfide, showed an increase of 0.2106 gram per gram of oxide. If the metal is monovalent, what is its atomic weight? $\text{O} = 16.00$; $\text{S} = 32.00$. If the metal is divalent, what is its atomic weight?

289. If 22.4 liters of oxygen, under standard conditions of pressure and temperature, weigh 32.00 grams and the same volume of hydrogen weighs 2.016 grams, what is the atomic weight of hydrogen?

Ans. 1.008.

290. If a liter of hydrogen, under standard conditions of pressure and temperature, weighs 0.08960 gram and a gram sample of pure zinc yielded, when treated with HCl , 344.0 cc. of hydrogen, what is the atomic weight of zinc?

291. A 0.5000-gram sample of a certain pure compound yielded 0.3195 gram of Cl_2 ; a 0.2368-gram portion of the salt on adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and ignition of the precipitate gave 0.1196 of CaO . What was the compound?

Ans. CaCl_2 .

292. The complete analysis of a certain pure salt gave the following results expressed as percentages: $\text{Cl} = 47.88$ per cent, $\text{N} = 6.31$ per cent, $\text{H} = 1.82$ per cent, $\text{Pt} = 43.94$ per cent. What is the empirical formula of the compound?

293. If, by an organic combustion, the percentage composition becomes established as 62.02 per cent carbon, 10.42 per cent hydrogen, and 27.56 per cent oxygen (by difference), what is the ratio carbon : hydrogen : oxygen? What is the empirical formula?

Ans. $\text{C}_3\text{H}_6\text{O}$.

294. A certain pure salt, which qualitative analysis showed to contain barium and chloride, on analysis of a 1.0000-gram sample yielded 1.120 grams of BaSO_4 and 1.377 grams of AgCl . What is the formula of the salt?

295. A chemist conducting an organic combustion analysis with an organic compound finds that, with a 1.0000-gram sample, 0.9777 gram of CO_2 and 0.2002 gram of water are obtained. Calculate the percentages of C , H and O in the sample and, from this, the atomic ratio of these elements. Give the empirical formula of the compound.

Ans. HCO_2 .

296. A certain copper mineral known as enargite was found on analysis to have the following composition: copper = 47.84 per cent; arsenic = 19.47 per cent; sulfur = 32.69 per cent. What is the formula of the mineral?

297. Give the empirical formula of the silicate mineral, the analysis of which gave the following results: SiO_2 = 55.12 per cent; K_2O = 21.53 per cent; and Al_2O_3 = 23.35 per cent.

Ans. KAlSi_2O_6 .

298. Given the formula of a pure compound as $\text{Zn}_2\text{P}_2\text{O}_7$. Calculate the percentage composition.

299. A certain salt mixture, of unknown composition, was treated with water with the result that a residue remained. This water-insoluble residue was identified as BaSO_4 . The filtrate from the water treatment was found to contain Na^+ and Cl^- . How may the application of quantitative analysis aid in determining whether the original mixture was BaCl_2 and Na_2SO_4 , or BaSO_4 and NaCl ?

300. A qualitative analysis of a certain sample showed the presence of iron and chloride. What would you do quantitatively to ascertain whether the compound was FeCl_2 or FeCl_3 ? Supply the necessary data on a 1-gram sample.

APPENDIX

TABLE V *

DENSITY OF STRONG ACIDS AT 15° C. IN VACUO
(According to Lunge, Isler, Naef, and Marchlewsky)

Specific Gravity at 15° 4° (Vacuo)	Per Cent by Weight			Specific Gravity at 15° 4° (Vacuo)	Per Cent by Weight	
	HCl	HNO ₃	H ₂ SO ₄		HNO ₃	H ₂ SO ₄
1.000	0.16	0.10	0.09	1.235	37.51	31.70
1.005	1.15	1.00	0.95	1.240	38.27	32.28
1.010	2.14	1.90	1.57	1.245	39.03	32.86
1.015	3.12	2.80	2.30	1.250	39.80	33.43
1.020	4.13	3.70	3.03	1.255	40.56	34.00
1.025	5.15	4.60	3.76	1.260	41.32	34.57
1.030	6.15	5.50	4.49	1.265	42.08	35.14
1.035	7.15	6.38	5.23	1.270	42.85	35.71
1.040	8.16	7.26	5.96	1.275	43.62	36.29
1.045	9.16	8.13	6.67	1.280	44.39	36.87
1.050	10.17	8.99	7.37	1.285	45.16	37.45
1.055	11.18	9.84	8.07	1.290	45.93	38.03
1.060	12.19	10.67	8.77	1.295	46.70	38.61
1.065	13.19	11.50	9.47	1.300	47.47	39.19
1.070	14.17	12.32	10.19	1.305	48.24	39.77
1.075	15.16	13.14	10.90	1.310	49.05	40.35
1.080	16.15	13.94	11.60	1.315	49.88	40.93
1.085	17.13	14.73	12.30	1.320	50.69	41.50
1.090	18.11	15.52	12.99	1.325	51.51	42.08
1.095	19.06	16.31	13.67	1.330	52.34	42.66
1.100	20.01	17.10	14.35	1.335	53.17	43.20
1.105	20.97	17.88	15.03	1.340	54.04	43.74
1.110	21.92	18.66	15.71	1.345	54.90	44.28
1.115	22.86	19.44	16.36	1.350	55.76	44.82
1.120	23.82	20.22	17.01	1.355	56.63	45.35
1.125	24.78	20.99	17.66	1.360	57.54	45.88
1.130	25.75	21.76	18.31	1.365	58.45	46.41
1.135	26.70	22.53	18.96	1.370	59.36	46.94
1.140	27.66	23.30	19.61	1.375	60.27	47.47
1.145	28.61	24.07	20.26	1.380	61.24	48.00
1.150	29.57	24.83	20.91	1.385	62.21	48.53
1.155	30.55	25.59	21.55	1.390	63.20	49.06
1.160	31.52	26.35	22.19	1.395	64.22	49.59
1.165	32.49	27.11	22.83	1.400	65.27	50.11
1.170	33.46	27.87	23.47	1.405	66.37	50.63
1.175	34.42	28.62	24.12	1.410	67.47	51.15
1.180	35.39	29.37	24.76	1.415	68.60	51.66
1.185	36.31	30.12	25.40	1.420	69.77	52.15
1.190	37.23	30.87	26.04	1.425	70.95	52.63
1.195	38.16	31.60	26.68	1.430	72.14	53.11
1.200	39.11	32.34	27.32	1.435	73.35	53.59
1.205	33.07	27.95	1.440	74.64	54.07
1.210	33.80	28.58	1.445	75.94	54.55
1.215	34.53	29.21	1.450	77.24	55.03
1.220	35.26	29.84	1.455	78.56	55.50
1.225	36.01	30.48	1.460	79.94	55.97
1.230	36.76	31.11	1.465	81.38	56.43

TABLE V—*Continued*

Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight HNO ₃	Per Cent by Weight H ₂ SO ₄	Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight H ₂ SO ₄	Specific Gravity at $\frac{15^\circ}{4^\circ}$ (Vacuo)	Per Cent by Weight H ₂ SO ₄
1.470	82.86	56.90	1.610	69.56	1.750	81.56
1.475	84.41	57.37	1.615	70.00	1.755	82.00
1.480	86.01	57.83	1.620	70.42	1.760	82.44
1.485	87.66	58.28	1.625	70.85	1.765	83.01
1.490	89.86	58.74	1.630	71.27	1.770	83.51
1.495	91.56	59.22	1.635	71.70	1.775	84.02
1.500	94.04	59.70	1.640	72.12	1.780	84.50
1.505	96.34	60.18	1.645	72.55	1.785	85.10
1.510	98.05	60.65	1.650	72.96	1.790	85.70
1.515	99.02	61.12	1.655	73.40	1.795	86.30
1.520	99.62	61.59	1.660	73.81	1.800	86.92
1.525	62.06	1.665	74.24	1.805	87.60
1.530	62.53	1.670	74.66	1.810	88.30
1.535	63.00	1.675	75.08	1.815	89.16
1.540	63.43	1.680	75.50	1.820	90.05
1.545	63.85	1.685	75.94	1.825	91.00
1.550	64.26	1.690	76.38	1.830	92.10
1.555	64.67	1.695	76.76	1.835	93.56
1.560	65.20	1.700	77.17	1.840	95.60
1.565	65.65	1.705	77.60	1.8405	95.95
1.570	66.09	1.710	78.04	1.8410	96.38
1.575	66.53	1.715	78.48	1.8415	97.35
1.580	66.95	1.720	78.92	1.8410	98.20
1.585	67.40	1.725	79.36	1.8405	98.52
1.590	67.83	1.730	79.80	1.8400	98.72
1.595	68.26	1.735	80.24	1.8395	98.77
1.600	68.70	1.740	80.68	1.8390	99.12
1.605	69.13	1.745	81.12	1.8385	99.31

* Taken from Treadwell-Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons. Reprinted with permission.

TABLE VI *

DENSITY AND PER CENT OF ACETIC ACID SOLUTIONS, 15° C.
(Oudemans)

15° C./4° C.	Per Cent by Weight	15° C./4° C.	Per Cent by Weight
0.9992	0	1.0615	50
1.0022	2	1.0631	52
1.0054	4	1.0646	54
1.0083	6	1.0660	56
1.0113	8	1.0673	58
1.0142	10	1.0685	60
1.0171	12	1.0697	62
1.0200	14	1.0707	64
1.0228	16	1.0717	66
1.0256	18	1.0725	68
1.0284	20	1.0733	70
1.0311	22	1.0740	72
1.0337	24	1.0744	74
1.0363	26	1.0747	76
1.0388	28	1.0748	78
1.0412	30	1.0748	80
1.0436	32	1.0746	82
1.0459	34	1.0742	84
1.0481	36	1.0736	86
1.0502	38	1.0726	88
1.0523	40	1.0713	90
1.0543	42	1.0696	92
1.0562	44	1.0674	94
1.0580	46	1.0644	96
1.0598	48	1.0604	98
1.0615	50	1.0553	100

* From Treadwell-Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons.
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TABLE VII *

DENSITY OF AMMONIA SOLUTIONS AT 15° C.

(According to Lunge and Wiernik)

Specific Gravity	Per Cent NH ₃	Specific Gravity	Per Cent NH ₃
1.000	0.00	0.940	15.63
0.998	0.45	0.938	16.22
0.996	0.91	0.936	16.82
0.994	1.37	0.934	17.42
0.992	1.84	0.932	18.03
0.990	2.31	0.930	18.64
0.988	2.80	0.928	19.25
0.986	3.30	0.926	19.87
0.984	3.80	0.924	20.49
0.982	4.30	0.922	21.12
0.980	4.80	0.920	21.75
0.978	5.30	0.918	22.39
0.976	5.80	0.916	23.03
0.974	6.30	0.914	23.68
0.972	6.80	0.912	24.33
0.970	7.31	0.910	24.99
0.968	7.82	0.908	25.65
0.966	8.33	0.906	26.31
0.964	8.84	0.904	26.98
0.962	9.35	0.902	27.65
0.960	9.91	0.900	28.33
0.958	10.47	0.898	29.01
0.956	11.03	0.896	29.69
0.954	11.60	0.894	30.37
0.952	12.17	0.892	31.05
0.950	12.74	0.890	31.75
0.948	13.31	0.888	32.50
0.946	13.88	0.886	33.25
0.944	14.46	0.884	34.10
0.942	15.04	0.882	34.95

* Taken from Treadwell-Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons. Reprinted with permission.

TABLE VIII *

SPECIFIC GRAVITY OF POTASSIUM AND SODIUM HYDROXIDE
SOLUTIONS AT 15° C.

Specific Gravity	Per Cent KOH	Per Cent NaOH	Specific Gravity	Per Cent KOH	Per Cent NaOH
1.007	0.9	0.61	1.252	27.0	22.64
1.014	1.7	1.20	1.263	28.2	23.67
1.022	2.6	2.00	1.274	28.9	24.81
1.029	3.5	2.71	1.285	29.8	25.80
1.037	4.5	3.35	1.297	30.7	26.83
1.045	5.6	4.00	1.308	31.8	27.80
1.052	6.4	4.64	1.320	32.7	28.83
1.060	7.4	5.29	1.332	33.7	29.93
1.067	8.2	5.87	1.345	34.9	31.22
1.075	9.2	6.55	1.357	35.9	32.47
1.083	10.1	7.31	1.370	36.9	33.69
1.091	10.9	8.00	1.383	37.8	34.96
1.100	12.0	8.68	1.397	38.9	36.25
1.108	12.9	9.42	1.410	39.9	37.47
1.116	13.8	10.06	1.424	40.9	38.80
1.125	14.8	10.97	1.438	42.1	39.99
1.134	15.7	11.84	1.453	43.4	41.41
1.142	16.5	12.64	1.468	44.6	42.83
1.152	17.6	13.55	1.483	45.8	44.38
1.162	18.6	14.37	1.498	47.1	46.15
1.171	19.5	15.13	1.514	48.3	47.60
1.180	20.5	15.91	1.530	49.4	49.02
1.190	21.4	16.77	1.546	50.6	
1.200	22.4	17.67	1.563	51.9	
1.210	23.3	18.58	1.580	53.2	
1.220	24.2	19.58	1.597	54.5	
1.231	25.1	20.59	1.615	55.9	
1.241	26.1	21.42	1.634	57.5	

* From Treadwell-Hall, *Analytical Chemistry*, Vol. II, published by John Wiley & Sons.
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APPENDIX

TABLE IX

DENSITY OF WATER

Temperature, Deg. C.	Density	Temperature, Deg. C.	Density	Temperature, Deg. C.	Density
0	0.99987	22	780	43	107
1	993	23	756	44	066
2	997	24	732	45	0.99025
3	999	25	0.99707	46	0.98982
4	1.00000	26	681	47	940
5	0.99999	27	654	48	896
6	997	28	626	49	852
7	993	29	597	50	0.98807
8	988	30	0.99567	51	762
9	981	31	537	52	715
10	0.99973	32	505	53	669
11	963	33	473	54	621
12	952	34	440	55	0.98573
13	940	35	0.99406	60	324
14	927	36	371	65	059
15	0.99913	37	336	70	0.97781
16	897	38	299	75	489
17	880	39	262	80	0.97183
18	862	40	0.99224	85	0.96865
19	843	41	186	90	534
20	C.99823	42	147	95	192
21	802				

TABLE X

PERCENTAGE IONIZATION OF COMMON ACIDS, BASES AND SALTS IN
0.1 M SOLUTION AT 18° C.

Acid	Ionization Reaction	Per Cent Ionized
Hydrochloric.....	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	92.0
Nitric.....	$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	92.0
Nitrous.....	$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	8.0
Formic.....	$\text{HCHO}_2 \rightleftharpoons \text{H}^+ + \text{CHO}_2^-$	4.5
Acetic.....	$\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^-$	1.34
Hydrocyanic.....	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	0.01
Sulfuric.....	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	90.0
	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{--}$	60.0
Oxalic.....	$\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^-$	40.0
	$\text{HC}_2\text{O}_4^- \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{--}$	1.0
Carbonic.....	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	0.12
	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$	0.0017
Hydrosulfuric.....	$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$	0.05
	$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{--}$	0.0001
Phosphoric.....	$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$	27.0
	$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{--}$	0.1
	$\text{HPO}_4^{--} \rightleftharpoons \text{H}^+ + \text{PO}_4^{---}$	0.0001
Water.....	$\text{HOH} \rightleftharpoons \text{H}^+ + \text{OH}^-$	0.0000002
Base		
Sodium hydroxide.....	$\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$	90.5
Ammonium hydroxide....	$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.31
Calcium hydroxide.....	$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{OH}^-$	75.0
Salt	Examples	
Uni-univalent.....	$\text{KCl}, \text{NaNO}_3, \text{NH}_4\text{Cl}, \text{NaC}_2\text{H}_3\text{O}_2$	80.-85.
Uni-bivalent.....	$\text{CaCl}_2, \text{K}_2\text{SO}_4, \text{etc.}$	70.-75.
Bi-bivalent.....	$\text{MgSO}_4, \text{CuSO}_4, \text{etc.}$	35.-45.

TABLE XI
IONIZATION CONSTANTS

Electrolyte	Primary	Secondary	Tertiary
HCl.....	*		
HNO ₃	*		
HNO ₂	4.5×10^{-4}		
HCHO ₂	2×10^{-4}		
HC ₂ H ₃ O ₂	1.8×10^{-5}		
HCN.....	2.1×10^{-9}		
H ₂ SO ₄	*	3×10^{-2}	
H ₂ C ₂ O ₄	3.8×10^{-2}	5×10^{-5}	
H ₂ C ₄ H ₄ O ₆	1.1×10^{-3}	6.9×10^{-5}	
H ₂ SO ₃	1.7×10^{-2}	5×10^{-6}	
H ₂ CO ₃	3×10^{-7}	7×10^{-11}	
H ₂ S †.....	9×10^{-8}	1.2×10^{-15}	
H ₃ AsO ₄	4.5×10^{-3}	4×10^{-5}	6×10^{-10}
H ₃ PO ₄	7.5×10^{-3}	6.3×10^{-8}	3.6×10^{-13}
H ₃ AsO ₃	2.1×10^{-8}		
H ₃ BO ₃	1.1×10^{-9}		
HOH ‡.....	2×10^{-16}		
NaOH.....	*		
NH ₄ OH.....	1.75×10^{-5}		
Ca(OH) ₂	3×10^{-2}		

* Ionization too great to yield an ionization constant.

$$\dagger \frac{(C_{\text{H}^+})^2 \times C_{\text{S}^-}}{C_{\text{H}_2\text{S}}} = 1.1 \times 10^{-22}; (C_{\text{H}^+})^2 + C_{\text{S}^-} = 1.1 \times 10^{-23}.$$

$$\ddagger C_{\text{H}^+} \times C_{\text{OH}^-} = 1.2 \times 10^{-14}.$$

TABLE XII.—SOLUBILITY OF BASES AND SALTS IN WATER AT 18° C.

	Li	Na	K	Mg	Ca	Br	Ba	Fe ⁺⁺	Cu ⁺⁺	Zn	Pb	Ag	Hg ⁺	Hg ²⁺
F	0.37 0.1042	4 1.048	92.3 15.86-2 aq.	0.0076** 0.0014	0.0016 0.0208	0.018* 0.038	0.018* 0.038	*		1.6 0.155-4 aq.	0.0041* 0.0026	185 14.32	Decomp.	Decomp.
Cl	77.0 18.16	35.9 6.14	33.4 4.48	54.1 5.68-6 aq.	72.5 6.54-6 aq.	52.8 3.33-6 aq.	35.2 3.33-6 aq.	41.5 2.76-12 aq.	75.6 5.62-2 aq.	362 26.54-11 aq.	0.015** 0.0329	0.045** 0.0011	0.042** 0.0045	7.39 0.273
Br	174.0 20.02	89.0 8.65-2 aq.	64.1 5.21-6 aq.	96.1 5.21-6 aq.	141 7.03-6 aq.	98 3.96-6 aq.	103 3.46-2 aq.	53.5 2.48-6 aq.	v.s. -4 aq.	441 19.59-2 aq.	0.894* 0.0219	0.045** 0.0045	0.045** 0.0011	0.4 0.011
I	163.0 12.17	176.7 11.79-2 aq.	142.6 8.59	145 5.32-8 aq.	203 6.91-6 aq.	175 5.16-6 aq.	195 3.46-2 aq.	*		422 13.55	0.086 0.0014	0.037** 0.013	0.037** 0.013	**
CO ₃	213.5 23.6	97.0 9.11	6.7 0.548	1.0 6.80-6 aq.	177.8 8.53-2 aq.	175.0 6.88	35.5 1.66-1 aq.	*	104 7.12-1 aq.	138.8 8.53-4 aq.	151.3 4.05-1 aq.	107 0.52	Decomp.	Decomp.
BrO ₃	153.7 11.4	34.0 2.25	6.5 0.389	*	85 2.87-1 aq.	33 0.95-1 aq.	0.61 0.0158-1 aq.	*		57.5	1.34 0.029	0.144* 0.0061	Decomp.	16
IO ₃	80.3 4.41	8.5 0.429	7.5 0.350	8.22 0.22-1 aq.	0.26* 0.0067-6 aq.	0.028* 0.036	0.021* 0.043-1 aq.	*	0.121* 0.0033	0.9* 0.022	0.0019** 0.034	0.004** 0.014	**	**
NO ₃	10.19-3 aq.	56.0 10.11	20.6 2.93	73.2 4.94-6 aq.	121.2 7.39-4 aq.	67.6 3.20-4 aq.	8.8 0.336	46.5 (24°) 2.53-9 aq.	120 6.40-6 aq.	115.1 6.08-6 aq.	50.7 1.532	204 12.0	v.s.	v.s.
SO ₄	34.3 3.12-1 aq.	16.8 1.182-10 aq.	10.73 0.616	34.6 2.85-7 aq.	0.202* 0.015-2 aq.	0.0114** 0.062	0.023** 0.039	26.4 1.74-7 aq.	19.9 1.25-5 aq.	53.0 2.28-7 aq.	0.0041** 0.014	0.775 0.0248	Decomp.	Decomp.
CrO ₄	110.9 8.54-2 aq.	77.5 4.78-6 aq.	62.8 3.23	72.3 5.13-7 aq.	2.34 0.150	0.12* 0.0039	0.038** 0.015	0.022* 0.0012-2 aq.	**	**	0.028* 0.062	0.0025** 0.076	Decomp.	Decomp.
CrO ₆	6.24 (25°) 0.612	3.5 0.261	37.7 (25°) 2.27-1 aq.	0.03* 0.0027-2 aq.	0.056** 0.044	0.0045** 0.026	0.0089 0.036		**	0.064** 0.051	0.0035 0.012	0.0035 0.012	**	**
CO ₂	1.35 0.1823	19.5 1.840-10 aq.	111.5 8.08	0.093* 0.0113-3 aq.	0.0013** 0.013	0.001** 0.068	0.0022** 0.011	**	Decomp.	0.001** 0.081	0.0311** 0.041	0.003** 0.011	**	**
C ₂ H ₃ O ₂	v.s. -2 aq.	47 5.73-3 aq.	245 25.0	v.s. -4 aq.	35.0 2.21-2 aq.	*	2.7-3 aq.	*	0.0022* 0.0012	40 (25°) 3.21-2 aq.	50 (25°) 1.538-3 aq.	1.005 0.0602	0.75 (13°) 0.029*	
OH	12.8 5.32-1 aq.	107.5 26.9-1 aq.	110 19.6-2 aq.	0.084 0.015	0.167 0.023	0.75 0.063-8 aq.	3.58 0.210-8 aq.	0.067 0.03	**	0.058** 0.056	0.0155* 0.064	0.0022** 0.013	**	**
PO ₄	**	19.6 1.18-12 aq.	v.s.	*	**	**	*	**	**	-4 aq.	**	0.0064** 0.013	**	**

The upper number gives the number of grams of solute (calculated as anhydrous) that will dissolve in 100 g. of water at 18° C. The lower number gives the number of moles of solute in 1000 g. of water. If the solid in equilibrium with the saturated solution is a definite hydrate, the symbol aq., preceded by a figure, indicates the number of molecules of water of hydration.

The figures for the solubilities of slightly soluble substances have been abbreviated; thus, 0.0415 means 0.00015. A star means a slightly soluble substance—solubility less than about 1 g. in 100 g. of water. A double star means an "insoluble" substance—solubility less than about 0.01 g. in 100 g. of water.

s. means soluble; v.s. means very soluble.

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TABLE XIII
SOLUBILITY PRODUCT CONSTANTS

Compound	Solubility Product Constant	Compound	Solubility Product Constant
AgCl.....	1.1×10^{-10}	Hg ₂ Br ₂	1.3×10^{-21}
AgBr.....	3.5×10^{-13}	Hg ₂ I ₂	1.1×10^{-28}
AgI.....	1.7×10^{-16}	HgS.....	4.0×10^{-53}
AgCNS.....	7.1×10^{-13}	MgCO ₃	2.6×10^{-5}
Ag ₂ CrO ₄	1.7×10^{-12}	MgNH ₄ PO ₄	2.5×10^{-13}
Ag ₂ SO ₄	7.0×10^{-13}	Mg(OH) ₂	3.5×10^{-11}
Ag ₃ PO ₄	1.6×10^{-18}	Mn(OH) ₂	4.0×10^{-14}
BaCO ₃	1.8×10^{-9}	MnS.....	1.4×10^{-15}
BaCrO ₄	2.3×10^{-10}	NiS.....	1.4×10^{-24}
BaSO ₄	1.2×10^{-10}	PbCl ₂	2.4×10^{-4}
CaCO ₃	1.7×10^{-8}	PbBr ₂	7.4×10^{-5}
CaC ₂ O ₄	3.9×10^{-9}	PbI ₂	1.3×10^{-8}
CaCrO ₄	2.3×10^{-2}	PbCO ₃	1.7×10^{-11}
CaSO ₄	2.2×10^{-4}	PbCrO ₄	1.7×10^{-14}
CdS.....	3.6×10^{-29}	PbS.....	4.2×10^{-28}
CoS.....	3.0×10^{-26}	PbSO ₄	2.3×10^{-8}
Cu ₂ I ₂	2.6×10^{-12}	SrCO ₃	4.6×10^{-9}
CuS.....	8.5×10^{-45}	SrC ₂ O ₄	1.4×10^{-7}
Fe(OH) ₂	1.6×10^{-14}	SrSO ₄	3.6×10^{-7}
Fe(OH) ₃	1.1×10^{-36}	Zn(OH) ₂	1.0×10^{-18}
FeS.....	1.5×10^{-19}	ZnS.....	1.2×10^{-23}
Hg ₂ Cl ₂	2.0×10^{-18}		

TABLE XIV
POTENTIAL SERIES

Electrode Reaction	Molal Potential in Volts at 25° C.	
$K \rightleftharpoons K^+$	+1e	-2.922
$Ba \rightleftharpoons Ba^{++}$	+2e	-2.90
$Sr \rightleftharpoons Sr^{++}$	+2e	-2.89
$Ca \rightleftharpoons Ca^{++}$	+2e	-2.87
$Na \rightleftharpoons Na^+$	+1e	-2.712
$Mg \rightleftharpoons Mg^{++}$	+2e	-2.34
$Al \rightleftharpoons Al^{+++}$	+3e	(-1.67)
$Mn \rightleftharpoons Mn^{++}$	+2e	(-1.05)
$Zn \rightleftharpoons Zn^{++}$	+2e	-0.7620
$Cr \rightleftharpoons Cr^{+++}$	+3e	-0.71
$S^- \rightleftharpoons S$	+2e	-0.508 (basic); 0.141 (acid)
$Fe \rightleftharpoons Fe^{++}$	+2e	-0.440
$Cd \rightleftharpoons Cd^{++}$	+2e	-0.4020
$Co \rightleftharpoons Co^{++}$	+2e	(-0.277)
$Ni \rightleftharpoons Ni^{++}$	+2e	(-0.250)
$Sn \rightleftharpoons Sn^{++}$	+2e	-0.136
$Pb \rightleftharpoons Pb^{++}$	+2e	-0.126
$Fe \rightleftharpoons Fe^{+++}$	+3e	-0.036
$H_2 \rightleftharpoons 2H^+$	+2e	0.00
$Cu^+ \rightleftharpoons Cu^{++}$	+1e	+0.167
$Sn^{++} \rightleftharpoons Sn^{++++}$	+2e	+0.15
$H_2O + Sb \rightleftharpoons SbO^+ + 2H^+$	+3e	(+0.212)
$H_2O + Bi \rightleftharpoons BiO^+ + 2H^+$	+3e	(+0.32)
$2H_2O + As \rightleftharpoons HAsO_2(aq.) + 3H^+$	+3e	(+0.2475)
$Cu \rightleftharpoons Cu^{++}$	+2e	+0.3448
$4OH^- \rightleftharpoons O_2 + 2H_2O$	+4e	+0.401
$Fe(CN)_6^{--} \rightleftharpoons Fe(CN)_6^{=}$	+1e	+0.36
$Cu \rightleftharpoons Cu^+$	+1e	+0.522
$MnO_2 + 4OH^- \rightleftharpoons MnO_4^- + 2H_2O$	+3e	+0.58
$2I^- \rightleftharpoons I_2$	+2e	+0.5345
$HAsO_2 + 2H_2O \rightleftharpoons H_3AsO_4 + 2H^+$	+2e	+0.559
$Fe^{++} \rightleftharpoons Fe^{+++}$	+1e	+0.771
$2Hg \rightleftharpoons Hg_2^{++}$	+2e	+0.7986
$Ag \rightleftharpoons Ag^+$	+1e	+0.7995
$Hg \rightleftharpoons Hg^{++}$	+2e	+0.854
$Hg_2^{++} \rightleftharpoons 2Hg^{++}$	+2e	+0.910
$NO + 2H_2O \rightleftharpoons NO_3^- + 4H^+$	+3e	+0.96
$2Br^- \rightleftharpoons Br_2$	+2e	+1.0652
$Au^+ \rightleftharpoons Au^{+++}$	+2e	+ca. 1.29
$2Cr^{+++} + 3H_2O \rightleftharpoons Cr_2O_7 + 14H^+$	+6e	+1.36
$2Cl^- \rightleftharpoons Cl_2$	+2e	+1.3583
$Au \rightleftharpoons Au^{+++}$	+3e	+1.42
$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+$	+5e	+1.52

TABLE XV

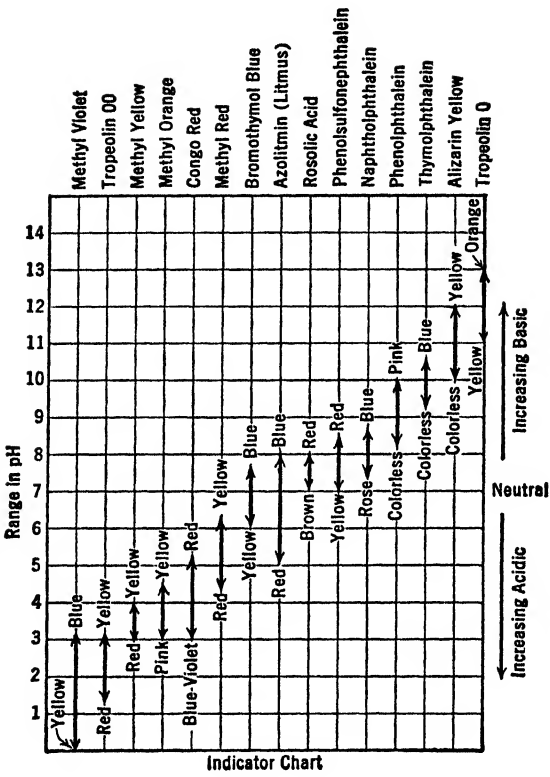


TABLE XVI
PERIODIC TABLE OF THE ELEMENTS

Group	0	I	II	III	IV	V	VI	VII	VIII
Type Formulas		R ₂ - RH	RO - RH ₂	R ₂ O ₃ - RH ₃	RO ₂ - RH ₄	R ₂ O ₅ - RH ₅	RO ₃ - H ₂ R	R ₂ O ₇ - HR	
Series 1		H 1.0078							
2	He 4.002	Li 6.940	Be 9.02	B 10.82	C 12.000	N 14.008	O 16.000	F 19.00	
3	Ne 20.183	Na 22.997	Mg 24.32	Al 26.97	Si 28.06	P 31.02	S 32.06	Cl 35.457	
4	A 39.444	K 39.096	Ca 40.08	Sc 45.10	Ti 47.90	V 50.95	Cr 52.01	Mn 54.93	Fe 55.84 Co 58.94 Ni 58.69
5		Cu 63.57	Zn 65.38	Ga 69.72	Ge 72.6	As 74.91	Se 78.96	Br 79.916	
6	Kr 83.7	Rb 85.44	Sr 87.63	Yt 88.92	Zr 91.22	Cb 92.91	Mo 96.0		Ru 101.7 Rh 102.91 Pd 106.7
7		Ag 107.880	Cd 112.41	In 114.76	Sn 118.70	Sb 121.76	Te 127.61	I 126.92	
8	Xe 131.3	Cs 132.91	Ba 137.36	La 138.92	Ce 140.13	[Positions between of the rare earth group]			
9				brackets occupied by elements					
10			not yet definitely assigned.]		Hf 178.6	Ta 181.4	W 184.0		Os 191.5 Ir 193.1 Pt 195.23
11		Au 197.2	Hg 200.61	Tl 204.39	Pb 207.22	B 209.00			
12	Rn 222.0		Ra 226.97		Th 232.12		U 238.14		

TABLE XVII
NORMAL SOLUTIONS OF ACIDS AND BASES

Reagent	Molecular Weight	Normal Soln. Contains gm/liter	Millicquivalent gm/cc
CH ₃ COOH	60.03	60.03	0.06003
H ₃ BO ₃	61.84	61.84	0.06184
HBr	80.92	80.92	0.08092
HCl	36.46	36.46	0.03646
H ₂ C ₂ O ₄	90.036	45.018	0.05303
H ₃ PO ₄	98.04	49.02	0.04902
H ₂ SO ₄	98.08	49.04	0.04904
NH ₄ OH	35.05	35.05	0.03505
Ba(OH) ₂ ·8H ₂ O	315.50	157.75	0.15775
Ca(OH) ₂	74.09	37.05	0.03705
KOH	56.1	56.1	0.0561
K ₂ CO ₃	138.20	69.10	0.06910
Na ₂ CO ₃	106.00	53.00	0.05300
NaOH	40.00	40.00	0.04000
Na ₂ B ₄ O ₇	201.43	100.72	0.10072
Na ₂ B ₄ O ₇
10H ₂ O	381.43	190.72	0.19072

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TABLE XVIII
NORMAL SOLUTIONS OF PRECIPITATING AGENTS

Formula	Molecular Weight	Normal Soln. Contains gm/liter	Millicquivalent gm/cc
NH ₄ SCN	76.11	76.11	0.07611
HCl	36.46	36.46	0.03646
K ₄ Fe(CN) ₆	368.26	368.26	0.36826
K ₄ Fe(CN) ₆ ·3H ₂ O	422.33	422.33	0.42233
KSCN	97.17	97.17	0.09717
AgNO ₃	169.89	169.89	0.16989
NaCl	58.45	58.45	0.05845

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TABLE XIX

NORMAL SOLUTIONS OF OXIDIZING AND REDUCING AGENTS

Reagent	Molecular Weight	Normal Soln. Contains gm/liter	Millicequiv- alent gm/cc
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	142.09	71.05	0.07105
H_3AsO_3	125.93	62.97	0.06297
As_2O_3	197.82	49.46	0.04946
Br	79.916	79.916	0.07992
$\text{Ca}(\text{OCl})_2$	126.99	63.50	0.06350
Cl	35.457	35.457	0.03546
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.02	278.02	0.27802
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	392.14	392.14	0.39214
H_2O_2	34.02	17.01	0.01701
H_2S	34.08	17.04	0.01704
I	126.92	126.92	0.12692
$\text{H}_2\text{C}_2\text{O}_4$	90.036	45.018	0.04502
$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	126.05	63.03	0.06303
KBrO_3	167.02	27.84	0.02784
$\text{K}_2\text{Cr}_2\text{O}_7$	294.21	49.04	0.04904
KIO_3	214.03	35.67	0.03567
KMnO_4	158.03	31.61	0.03161
$\text{Na}_2\text{S}_2\text{O}_3$	158.11	158.11	0.15811
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	248.19	248.19	0.24819
$\text{Na}_2\text{C}_2\text{O}_4$	133.99	66.995	0.067
SnCl_2	189.61	94.80	0.0948
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	225.65	112.83	0.11283

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TABLE XX
CHEMICAL FACTORS

Sought	Found	Factor	Log	Sought	Found	Factor	Log
Ag	AgBr.....	0.5744	9.7593	Ba	BaCl ₂ ·2H ₂ O...	0.5621	9.7498
	AgCl.....	0.7526	9.8766		BaCO ₃	0.6961	9.8426
	AgCN.....	0.8055	9.9060		BaCrO ₄	0.5422	9.7341
	AgI.....	0.4595	9.6622		BaSO ₄	0.5885	9.7697
	AgNO ₃	0.6350	9.8028		BaSiF ₆	0.4912	9.6013
	Ag ₂ O.....	0.8706	9.9398	BaO	BaCO ₃	0.7771	9.8905
	Ag ₃ PO ₄	0.7731	9.8882		BaCrO ₄	0.6053	9.7820
	Ag ₄ P ₂ O ₇	0.7125	9.8528		BaSO ₄	0.6570	9.8176
Al	Al ₂ O ₃	0.5294	9.7238	Ca	CaCl ₂	0.3612	9.5577
	AlPO ₄	0.2212	9.3449		CaCO ₃	0.4005	9.6025
Al ₂ O ₃	AlPO ₄	0.4179	9.6211		CaF ₂	0.5133	9.7103
As	As ₂ O ₃	0.7575	9.8794		CaO.....	0.7146	9.8541
	As ₂ O ₅	0.6521	9.8143		CaSO ₄	0.2944	9.4689
	As ₂ S ₃	0.6091	9.7847		CO ₂	0.9093	9.9587
	As ₂ S ₅	0.4832	9.6841	CaO	CaCO ₃	0.5603	9.7484
	Mg ₂ As ₂ O ₇	0.4827	9.6837		CaF ₂	0.7182	9.8563
	(NH ₄ MgAsO ₄) ₂ · H ₂ O.....	0.3939	9.5953		Ca(HCO ₃) ₂ ...	0.3459	9.5389
As ₂ O ₃	As ₂ O ₃	0.8609	9.9349		Ca(H ₂ PO ₄) ₂ ...	0.2394	9.3791
	As ₂ S ₃	0.8041	9.9053		CaH ₂ P ₂ O ₇ ...	0.2594	9.4140
	As ₂ S ₅	0.6378	9.8047		Ca(HSO ₃) ₂ ...	0.2773	9.4430
	Mg ₂ As ₂ O ₇	0.6372	9.8043		Ca ₃ (PO ₄) ₂ ...	0.5421	9.7341
	(NH ₄ MgAsO ₄) ₂ · H ₂ O.....	0.5199	9.7160		CaSO ₃	0.4667	9.6691
					CaSO ₄	0.4120	9.6149
BaCO ₃	BaSO ₄	0.8458	9.9272		CaSO ₄ ·2H ₂ O...	0.3257	9.5128
BaCl ₂ ·2H ₂ O	BaSO ₄	1.047	0.0198		CO ₂	1.274	9.1053
BaCrO ₄	BaSO ₄	1.085	0.0356	Cd	CdO.....	0.8754	9.9422
BaF ₂	BaSiF ₆	0.6271	9.7973		CdS.....	0.7780	9.8910
Ba(NO ₃) ₂	BaSO ₄	1.120	0.0491		CdSO ₄	0.6159	9.7895
Ba ₃ (PO ₄) ₂	BaSO ₄	0.8509	9.9345	Bi ₂ O ₃	Bi.....	1.115	0.0472
BaS	BaSO ₄	0.7258	9.8608		BiOCl.....	0.8946	9.9516
Bi	Bi ₂ O ₃	0.8970	9.9528		BiPO ₄	0.7663	0.8844
	BiOCl.....	0.8024	9.9044		Bi ₂ S ₃	0.9063	0.9573
	BiPO ₄	0.6874	9.8372		BiAsO ₄	0.6696	0.8258
	Bi ₂ S ₃	0.8129	9.9101		BiONO ₃	0.8118	9.9095
	BiAsO ₄	0.6006	9.7786		Bi(NO ₃) ₃ ·5H ₂ O	0.4803	9.6815
As ₂ O ₅	As ₂ S ₃	0.9341	9.9704	Br	Ag.....	0.7408	9.8697
	As ₂ S ₅	0.7410	1.8698		AgBr.....	0.4256	9.6290
	Mg ₂ As ₂ O ₇	0.7403	1.8694		AgCl.....	0.5576	9.7463
	(NH ₄ MgAsO ₄) ₂ · H ₂ O.....	0.6040	9.7810	C	HBr.....	0.9874	9.9945
					CO ₂	0.2727	9.4357
B	B ₂ O ₃	0.3123	9.4946		BaCO ₃	0.0608	8.7839
	KBF ₄	0.08651	8.9371	Cl	Ag.....	0.3287	9.5168
	H ₂ BO ₃	0.1761	9.2456		AgCl.....	0.2474	9.3934
	Na ₂ B ₄ O ₇ ·10H ₂ O	0.1142	9.0577		AgNO ₃	0.2088	9.3198
					HCl.....	0.9724	9.9879

TABLE XX—Continued

CHEMICAL FACTORS

Sought	Found	Factor	Log	Sought	Found	Factor	Log
Cl	I.....	0.2794	9.4462	F	BaSiF ₆	0.4076	9.6102
	KCl.....	0.4756	9.6772		CaF ₂	0.4866	9.6872
	MnO ₂	0.8158	9.9116		CaSO ₄	0.2791	9.4457
	NaCl.....	0.6066	9.7829		HF.....	0.9496	9.9776
	NH ₄ Cl.....	0.6628	9.8214		H ₂ SiF ₆	0.7910	9.8982
	RbCl.....	0.2933	9.4673		K ₂ SiF ₆	0.5170	9.7135
Co	Co(NO ₃) ₂ ·6H ₂ O	0.2026	9.3066	Fe	NaF.....	0.4524	9.6555
	K ₃ Co(NO ₂) ₆ ...	0.1304	9.1152		SiF ₄	0.7302	9.8634
	CoO.....	0.7866	9.8957		Fe ₂ O ₃	0.0994	9.8447
	Co ₃ O ₄	0.7344	9.8659	HF	FeCl ₂	0.4405	9.6440
	CoSO ₄	0.3804	9.5802		BaSiF ₆	0.4292	9.6327
	CoSO ₄ ·7H ₂ O...	0.2097	9.3216		CaF ₂	0.5126	9.7098
CoO	Co.....	1.2713	9.1043	Fe	CaSO ₄	0.2939	9.4682
	Co(NO ₃) ₂ ·6H ₂ O	0.2575	9.4109		F.....	1.053	0.0224
	K ₃ Co(NO ₂) ₆ ...	0.1657	9.2194		K ₂ SiF ₆	0.5449	9.7363
	Co ₃ O ₄	0.9336	9.9702		FeCl ₃ ·6H ₂ O....	0.2066	9.3152
	CoSO ₄	0.4836	9.6844		Fe(HCO ₃) ₂	0.3140	9.4969
	CoSO ₄ ·7H ₂ O...	0.2667	9.4259		FeO.....	0.7773	9.8906
Cr	BaCrO ₄	0.2052	9.3125	FeO	Fe ₂ O ₃	0.7236	9.8595
	Cr ₂ O ₃	0.6842	9.8352		FePO ₄	0.3701	9.5683
CdO	CdS.....	0.8888	9.9488		FeS.....	0.6352	9.8029
	Cd.....	1.142	0.0578		FeSO ₄	0.3676	0.5654
	CdSO ₄	0.6159	9.7895		FeSO ₄ ·7H ₂ O...	0.2008	9.3027
Cr	PbCrO ₄	0.1609	9.2067		FeSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O....	0.1424	9.1536
	K ₂ Cr ₂ O ₇	0.3535	9.5484		K ₂ Cr ₂ O ₇ (titration)....	1.139	0.0564
	K ₂ CrO ₄	0.1768	9.2474		Fe.....	1.287	0.1094
Cr ₂ O ₃	BaCrO ₄	0.3000	9.4771		FeCO ₃	0.6202	9.7925
	PbCrO ₄	0.2352	9.3715		Fe(HCO ₃) ₂	0.4039	9.6063
	CrO ₃	0.7602	9.8809		Fe ₂ O ₃	0.8098	9.9542
CrO ₄	BaCrO ₄	0.4578	9.6607		FePO ₄	0.4761	9.6777
	Cr ₂ O ₃	1.5263	9.1837		FeS.....	0.8172	9.9123
	PbCrO ₄	0.3589	9.5550		FeSO ₄	0.4729	9.6747
Cu	Cu ₂ O.....	0.8882	9.9485		FeSO ₄ ·7H ₂ O...	0.2584	9.4123
	CuO.....	0.7989	9.9025		FeSO ₄ (NH ₄) ₂ SO ₄ ·6H ₂ O....	0.1832	9.2630
	Cu ₂ S.....	0.7986	9.9023	Fe ₂ O ₃	Fe.....	1.430	0.1553
	Cu ₂ (CNS) ₂	0.5226	9.7181		FeCl ₃	0.4922	9.6922
	CuSO ₄	0.3982	9.6001		FeCO ₃	0.6892	9.8383
	CuSO ₄ ·5H ₂ O...	0.2546	9.4058		Fe ₃ O ₄	1.035	0.0149
					FePO ₄	0.5292	9.7237
					FeS.....	0.9082	9.9582
CuO	Cu.....	1.252	0.0975		FeS ₂	0.6655	9.8231
	Cu ₂ O.....	1.113	0.0463		Fe ₂ (SO ₄) ₃	0.3993	9.6013
	Cu ₂ S.....	0.9996	9.9998		(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O.	0.1656	0.2190
	Cu ₂ (CNS) ₂	0.6541	9.8166				
	CuSO ₄	0.4985	9.6976				
	CuSO ₄ ·5H ₂ O...	0.3186	9.5032				

TABLE XX—Continued

CHEMICAL FACTORS

Sought	Found	Factor	Log	Sought	Found	Factor	Log
HBr	Ag.....	0.7505	9.8754	K ₂ O	K ₂ SO ₄	0.5405	9.7328
	AgBr.....	0.4311	9.6346		KClO ₄	0.3399	9.5314
HCl					K ₂ PtCl ₆	0.1938	9.2873
	Ag.....	0.3380	9.5290		Pt.....	0.4826	9.6836
	AgCl.....	0.2544	9.4056	KClO ₄	AgCl.....	0.9667	9.9853
	CaCO ₃	0.7288	9.8626		KCl.....	1.858	0.2691
	KCl.....	0.4891	9.6894	H ₂ SO ₄	KOH.....	0.8740	9.9415
	K ₂ O.....	0.7743	9.8889		K ₂ SO ₄	0.5628	9.7503
	NaCl.....	0.6239	9.7951		Na ₂ CO ₃	0.9252	9.9662
	Na ₂ O.....	1.176	0.0705		Na ₂ C ₂ O ₄	0.7320	9.8645
	NH ₄ Cl.....	0.6817	9.8335		(NH ₄) ₂ SO ₄	0.7422	9.8705
	SnCl ₄	0.5600	9.7480	Hg	Hg ₂ Cl ₂	0.8495	9.9202
	Na ₂ CO ₃	0.6881	9.8377		HgCl ₂	9.7388	9.8686
	Methyl orange				HgO.....	0.9261	9.9666
	Na ₂ C ₂ O ₄				HgS.....	0.8620	9.9355
	standardization	0.5442	9.7358	I	Ag.....	1.177	9.0706
HI	Ag.....	1.186	0.0742		AgI.....	0.5406	9.7328
	AgI.....	0.5448	9.7362		KI.....	0.7645	9.8834
	Pd.....	2.398	0.3799		Pd.....	2.379	0.3764
	PdI ₂	0.7097	9.8510		PdI ₂	0.7041	9.8476
HNO ₃					Na ₂ S ₂ O ₃ ·5H ₂ O.....	0.5113	9.7087
	KNO ₃	0.6233	9.7947	K	AgCl.....	0.8855	9.9472
	N.....	4.498	0.6530		KCl.....	0.5244	9.7197
	NaNO ₃	0.7413	9.8700		K ₂ O.....	0.8300	9.9191
	NH ₃	3.701	0.5683		K ₂ SO ₄	0.4487	9.6520
	NH ₄ Cl.....	1.178	0.0711		KClO ₄	0.2822	9.4505
	(NH ₄) ₂ PtCl ₆	0.2838	9.4530		K ₂ PtCl ₆	0.1609	9.2064
	NO.....	2.100	0.3222		Pt.....	0.4006	9.6027
	N ₂ O ₃	0.658	0.2196	KCl	Ag.....	0.6911	9.8396
	N ₂ O ₄	1.370	0.1367		AgCl.....	0.5202	9.7162
	N ₂ O ₅	1.167	0.0671		K ₂ SO ₄	0.8557	9.9323
	C ₂₀ H ₁₆ N ₄ HNO ₃	0.1680	9.2252		KClO ₄	0.5381	9.7309
	Pt.....	0.6457	9.8100		K ₂ PtCl ₆	0.3067	9.4868
					Pt.....	0.7640	9.8831
H ₃ PO ₄	HPO ₃	1.225	0.0881	K ₂ O	KCl.....	0.6317	9.8005
	H ₄ P ₂ O ₇	1.101	0.0457				
	Mg ₂ P ₂ O ₇	0.8806	9.9448	Mo	MoO ₃	0.6667	9.8239
	P.....	3.159	0.4995		MoS ₃	0.4995	9.6985
	P ₂ O ₅	1.380	0.1399		MoS ₂	0.5996	9.7779
H ₂ S	BaSO ₄	0.1460	9.1644		PbMoO ₄	0.2615	9.4174
	CdS.....	0.2360	9.3729	N	HNO ₃	0.2223	9.3470
	FeS.....	0.3877	9.5885		NO ₂	0.3045	9.4835
	S.....	1.063	0.0265		N ₂ O ₃	0.3686	9.5665
H ₂ SO ₄					N ₂ O ₄	0.3045	9.4835
	Al ₂ (SO ₄) ₃	0.8594	9.9342				
	Ba(OH) ₂	0.5723	9.7576				
	BaSO ₄	0.4133	9.6163				
	K ₂ Al ₂ (SO ₄) ₄ · 24H ₂ O.....	0.3101	9.4915				
	K ₂ O.....	1.041	0.0174				

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